

# ORGANIC CHEMISTRY OF BIVALENT SULFUR

VOLUME III

*by*

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1960

CHEMICAL PUBLISHING CO., INC.

*212 Fifth Avenue, New York, N. Y.*

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CHEMICAL PUBLISHING CO., INC.

New York

N. Y.

Printed in the United States of America

Chemistry  
Library

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# Acknowledgments

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Publication of this work was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

It is a pleasure to express my gratitude also to the Freeport Sulfur Company for their grant.

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## CHAPTER 1.

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# Cyclic Sulfides

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Thiophene,  $\begin{array}{c} \text{CH:CH} \\ | \quad \diagup \\ \text{CH:CH} \end{array} \text{S}$ , the most important compound of this

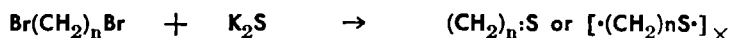
class, has been so extensively investigated that books have been written about it, the first by Victor Meyer, its discoverer,<sup>466</sup> another by Steinkopf<sup>641</sup> and the last by Hartough.<sup>311</sup> Reference should be made to these.

The striking parallelism between thiophene and benzene derivatives has interested chemists since the discovery of thiophene.<sup>215</sup> The recent production of thiophene on a commercial scale has led to increased activity in the investigation of its derivatives. It is being realized that they are distinctly different from the corresponding benzene derivatives.

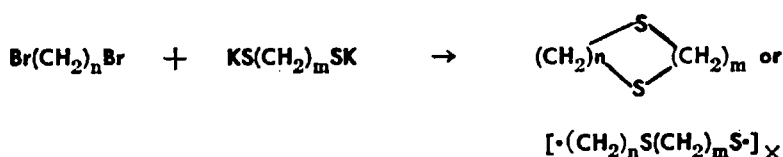
The chemistry of thiophene and its derivatives is so extensive and developing so fast that its coverage is beyond the scope of this book.

### General

The reaction of an alkyl dihalide with an alkaline sulfide may produce a cyclic sulfide or a linear polymer, or a mixture of the two, according to the number of intervening chain members:



The same statement holds when a dimercaptide is substituted for the sulfide:



As in other cases of cyclization, certain sizes of rings are favored. The large size of the sulfur atom may account for the fact that six membered rings are less favored than five membered. *n*-Pentane and sulfur give 2-methylthiophene.  $\beta,\beta'$ -Dichloroethyl sulfide and sodium sulfide give little of the cyclic monomer,  $\text{S}(\text{CH}_2\text{CH}_2)_2\text{S}$ , and much of the polymer while with dichloroethyl ether, thioxane,  $\text{O}(\text{CH}_2\text{CH}_2)_2\text{S}$ , is practically the sole product. The polymer predominates when ethylene bromide and ethylene mercaptan react in alkaline solution.<sup>282f</sup>

The percentage yields of rings of various sizes, from dihalides, dimercaptans, and sodium ethylate in alcohol solution, are given in Table 1.1. Because of the difficulties in isolating the cyclic compounds of high molecular weight, the yields given are doubtless low. The formation of rings of 8 to 11 members appears to be difficult. Dimers are formed along with monomers in some cases, and instead of them in others. Only a small amount of dimer appears along with the five membered ring.

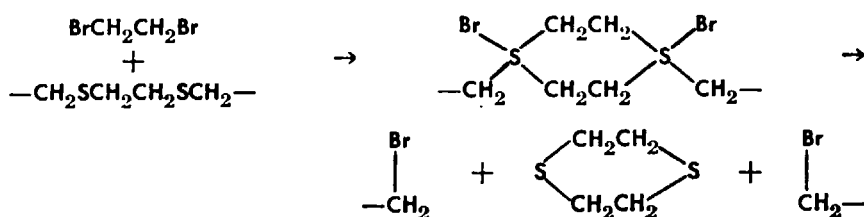
TABLE 1.1

*Yields of Rings of Different Sizes*

Dimercaptan	Dihalide	Monomer		Dimer	
		Size	Yield (%)	Size	Yield (%)
$\text{HS}(\text{CH}_2)_2\text{SH}$	$\text{CH}_2\text{Cl}_2$	5	26	10	0.2
"	$\text{Br}(\text{CH}_2)_2\text{Br}$	6	46	12	—
"	$\text{Br}(\text{CH}_2)_3\text{Br}$	7	9	14	1.
"	$\text{Br}(\text{CH}_2)_4\text{Br}$	8	—	16	0.2
"	$\text{Br}(\text{CH}_2)_5\text{Br}$	9	—	18	0.15
"	$\text{Br}(\text{CH}_2)_6\text{Br}$	10	0.06	20	—
"	$\text{O}(\text{CH}_2\text{CH}_2\text{Cl})_2$	9	—	18	1.4
$\text{HS}(\text{CH}_2)_3\text{SH}$	$\text{CH}_2\text{Cl}_2$	6	15	12	—
"	$\text{Br}(\text{CH}_2)_2\text{Br}$	7	8.2	14	—
"	$\text{Br}(\text{CH}_2)_3\text{Br}$	8	4	16	1
"	$\text{Br}(\text{CH}_2)_4\text{Br}$	9	0.6	18	1.8
"	$\text{Br}(\text{CH}_2)_5\text{Br}$	11	—	22	1.1
$\text{S}(\text{CH}_2\text{CH}_2\text{SH})_2$	$\text{Br}(\text{CH}_2)_2\text{Br}$	9	—	18	1.7

The yield of dithiane from ethylene mercaptan and ethylene bromide depends on the reaction temperature. At the boiling point of the alcoholic solution the yield is only 33% but at room temperature it is 46%.<sup>458, 671</sup>

Some, at least, of these two sulfur ring compounds can be made from the polymers. Ethylene sulfide polymers give dithiane when heated with ethylene bromide. This involves sulfonium addition:<sup>66</sup>



This reaction was applied to the polymers obtained as by-products in making the above cyclic compounds.<sup>458, 671</sup> The results are in Table 2.1.

TABLE 2.1

*Dithiane Obtained from Polymers and BrCH<sub>2</sub>CH<sub>2</sub>Br*

Structural Unit	% by Weight	% of Calculated
—CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> S—	51	43
—CH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> S—	65	65
—CH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> S—	25	28
—CH <sub>2</sub> CH <sub>2</sub> S(CH <sub>2</sub> ) <sub>6</sub> S—	21	31

The polymer —CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>S— gave a 30% yield of 1,3-dithiolane. Heating the same polymers with trimethylene bromide did not give any isolatable ring compounds.<sup>671</sup>

Depolymerization can be effected also by heating in an atmosphere of hydrogen chloride. The results with a number of polymers are in Table 3.1.<sup>458</sup>

Vigorous reduction of polymeric pentamethylene and hexamethylene sulfides gave hydrocarbons and hydrogen sulfide but no mercaptans.<sup>101d</sup>



TABLE 3.1

*Yields of Cyclic Products from Heating Polymers  
in Hydrogen Chloride*

Structural Unit	Product	
$-\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S}-$	1,4-dithiane	60%
$-\text{CH}_2\text{SCH}_2\text{CH}_2\text{S}-$	1,3-dithiolane	30%
$-\text{CH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S}-$	$\text{S}(\text{CH}_2\text{CH}_2)_2\text{SO}_2$	20% & 1,4-dithiane 15%
$-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{O}-$	thioxane	20% & 1,4-dithiane 10%
$-\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}-$	1,3-dithiane	40%
$-\text{CH}_2\text{CH}_2\text{S}(\text{CH}_2)_2\text{S}-$	1,4-dithiane	10%
$-(\text{CH}_2)_3\text{S}(\text{CH}_2)_4\text{S}-$	Tetramethylene sulfide	10%
$-(\text{CH}_2)_3\text{S}(\text{CH}_2)_5\text{S}-$	Pentamethylene sulfide	20%

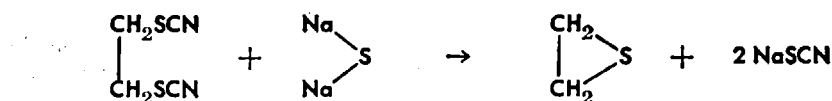
### Rings Containing One Sulfur Atom

#### EPISULFIDES



#### Formation

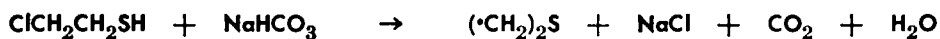
Ethylene sulfide, the simplest of the cyclic sulfides, is a special case both as to its formation and its reactions. It was first prepared by agitating ethylene dithiocyanate, or chlorothiocyanate,  $\text{ClCH}_2\text{CH}_2\text{SCN}$ , with a solution of sodium sulfide:



The volatile ethylene sulfide was carried over in a current of steam. Propylene and *i*-butene sulfides were prepared in the same way from propylene, *i*-butene, and  $\beta$ -methylbutene dithiocyanates.<sup>135, 186b, 187c, 188, 189</sup> The latter gives trimethylethylene sulfide.<sup>135</sup> The tetramethyl derivative has been made by the same reaction.<sup>713</sup> Dithiocyano-stearic and behenic acids have been converted into the corresponding sulfides.<sup>579</sup> 1,2-Dithiocyanocy-

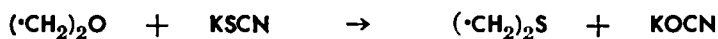
clohexane gives cyclohexene sulfide and 1-thiocyano-1-(thiocyanomethyl)-cyclohexane goes to epithiomethylenecyclohexane.<sup>494</sup>

Ethylene sulfide is produced in 50–90% yields by treating 2-chloroethyl mercaptan with a mild alkali:<sup>165, 510c</sup>



Cyclopentene sulfide is obtained similarly from 2-chlorocyclopentanethiol.<sup>675a</sup> The same treatment converts the acetates of mercapto-ethanol and of 2-mercapto-cyclohexanol to the corresponding sulfides.<sup>297, 468</sup>

A remarkably simple and efficient way to prepare ethylene sulfide has been discovered recently; the reaction of ethylene oxide with potassium thiocyanate:

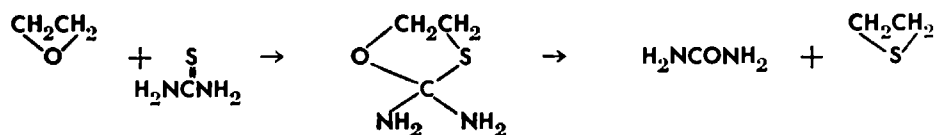


Ethylene oxide (30 g.) is passed into a solution of 45 g. potassium thiocyanate in 45 cc. of water at  $-10$  to  $-5^\circ$ . After several hours ethylene sulfide separates out as a layer. The yield based on the salt is said to be above 90%.<sup>110, 174, 178, 347b, 348</sup> Thiourea may be used instead of the thiocyanate.<sup>174, 257, 347b, 348</sup> Butadiene sulfide and 4-methylcyclohexene sulfide are obtained from the corresponding oxides and thiourea, but stilbene oxide goes to stilbene.<sup>173</sup> Styrene sulfide is obtained, however, from the oxide and potassium thiocyanate.<sup>292</sup>

This reaction was almost discovered some years earlier: ethylene oxide and thiourea were brought together in acetone solution and kept at room temperature for three weeks. A considerable amount of urea was isolated and mercaptoethanol, a hydrolysis product of ethylene sulfide, was shown to be present. From diphenylthiourea and ethylene oxide the addition product,  $\text{HOCH}_2\text{CH}_2\text{SC}(\text{:NPh})\text{NPh}$ , was isolated. Due to the presence of the two phenyl groups this is relatively stable. Its decomposition should give ethylene sulfide:

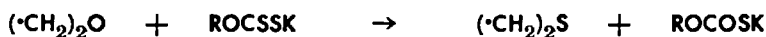


The reaction may be represented:



Hydrolysis of the assumed intermediate would give  $\text{HOCH}_2\text{-CH}_2\text{SC}(\text{:NH})\text{NH}_2$ . More detailed mechanisms have been proposed.<sup>175, 543</sup> In the presence of acid, an epoxide and thiourea give an isothiuronium salt which can be hydrolyzed.<sup>97</sup>

A xanthate, also, converts ethylene oxide to the sulfide:<sup>174</sup>



This can be formulated similarly. A study has been made of the yields of cyclic sulfides from a number of epoxides with thiourea, and with potassium and ammonium thiocyanates.<sup>174</sup> A good yield of the episulfide is obtained from cyclohexene oxide but none from cyclopentene oxide.<sup>97</sup>

A small amount of ethylene sulfide was formed when ethylene was bubbled through ethyl tetrasulfide at 140 to 150°. Propylene and cyclohexene gave 19 and 9%, respectively, of the sulfides when heated with ethyl tetrasulfide in a closed tube at 155°.<sup>356</sup>

Substituted ethylene sulfides can be made from the corresponding cyclic oxides and potassium thiocyanate in the same way. 2,2-Dimethylethylene sulfide is quite stable. The preparation of cyclohexene sulfide has been described in detail.<sup>675a, 675b</sup> It can be kept at 0° for several days.<sup>174, 631a</sup> Epichlorhydrin gives the corresponding cyclic sulfide, chloromethylethylene sulfide.<sup>174</sup> 1,2-Dithioglycerol, refluxed under a pressure of 10 mm. loses a molecule of water to form mercaptomethyl-ethylene sulfide:<sup>219, 399, 623</sup>



This mercaptan is obtained also by treating the acetate of dithioglycerol with a mild alkali.<sup>297</sup>

Infrared,<sup>293, 662</sup> Raman,<sup>662</sup> and micro-wave spectra<sup>176</sup> have been determined for ethylene sulfide. The dipole moment is 1.66 D.<sup>287</sup> One value of the C—S—C angle is 65° 48' <sup>176</sup> and another is 49° 30'.<sup>287</sup> From a study of the force constants the structure  $\text{H}_2\text{C}=\text{CH}_2$  is suggested.<sup>416</sup>



### Reactions

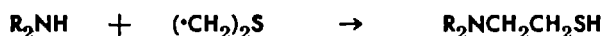
As the reactions of ethylene sulfide involve the breaking of a carbon-sulfur bond, they are discussed by Tarbell and Harnish.<sup>658</sup>

Ethylene sulfide polymerizes on standing several days. This is speeded up by acids or alkalis or by heating. Methyl iodide gives a crystalline compound, soluble in water, probably the sulfonium iodide. Ethylene sulfide is oxidised by nitric acid to a carboxysulfonic acid  $\text{HO}_2\text{CCH}_2\text{SO}_3\text{H}$ . With hydrochloric acid several products are formed,  $\text{HSCH}_2\text{CH}_2\text{Cl}$ ,  $\text{HSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ , and ethylene disulfide.<sup>188, 457</sup> Hydrobromic acid gives 2-bromoethyl mercaptan,  $\text{BrCH}_2\text{CH}_2\text{SH}$ .<sup>188</sup> The ring is opened up by phosphoric and phosphorous acids,<sup>1</sup> by acetic anhydride, and by acetyl chloride<sup>5, 205</sup> and iodide:<sup>350</sup>



Ethylene sulfide reacts with wool, apparently at the disulfide linkages.<sup>83</sup>

Primary and secondary amines react similarly: <sup>110, 374a, 349b, 567</sup>



The reaction may go further:



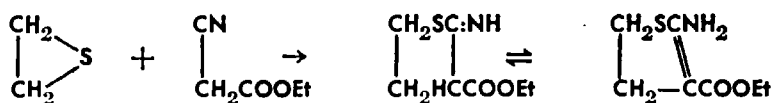
2-Mercaptoethylguanyllurea is formed from ethylene sulfide and guanyllurea.<sup>479b</sup> Isobutylene sulfide and heptylamine give the mercaptan,  $\text{C}_7\text{H}_{15}\text{NHCH}_2\text{CMe}_2\text{SH}$ . A similar mercaptan,  $(\text{CH}_2)_5\text{NCH}_2\text{CMe}_2\text{SH}$ , is from piperidine.<sup>630c</sup>

Propylene sulfide and hydrochloric acid give 1-chloro-2-mercaptopropane.<sup>189, 647</sup> With potassium hydrosulfide, 1,2-propanedithiol is formed.<sup>173</sup> With acetyl chloride, the yield of 2-chloropropyl thioacetate is quantitative.<sup>179</sup> Bromine and chlorine cleave propylene sulfide at the primary carbon giving the secondary disulfides,  $(\text{BrCH}_2\text{CHMeS}\cdot)_2$  and  $(\text{ClCH}_2\text{CHMeS}\cdot)_2$ , while with hydrogen peroxide the secondary bond is broken with the formation of a primary sulfonic acid,  $\text{MeCH}(\text{OH})\text{CH}_2\text{SO}_3\text{H}$ .<sup>648</sup>

Isobutylene sulfide and an alcohol react in two ways. The chief product is the primary mercaptan,  $\text{Me}_2\text{C}(\text{OR})\text{CH}_2\text{SH}$ , but there is some of the tertiary,  $\text{Me}_2\text{C}(\text{SH})\text{CH}_2\text{OR}$ .<sup>630a, 630b, 631b</sup> Olefin sulfides react with mercaptans only in the presence of a catalyst such as sodium ethylate or boron trifluoride.<sup>630a, 631b</sup> As with the alcohols, two products are formed,  $\text{Me}_2\text{C}(\text{SR})\text{CH}_2\text{SH}$  and  $\text{Me}_2\text{C}(\text{SH})\text{CH}_2\text{SR}$ . Cyclohexene sulfide gives 2-alkylmer-

capto cyclohexyl mercaptan.<sup>173, 631b</sup> A number of compounds of this class have been prepared. The reaction may be carried on in an inert solvent.<sup>566</sup> Tetramethylethylene sulfide does not react with mercaptans.<sup>631b</sup> Isobutylene sulfide and acetic anhydride give a mixture of the two possible diacetyl derivatives.<sup>179</sup>

Olefin sulfides react with cyanoacetic ester to give tautomeric cyclic esters: <sup>629</sup>



Ethylene sulfide condenses with cyanamide to a product which is said to have insecticidal properties.<sup>479a</sup>

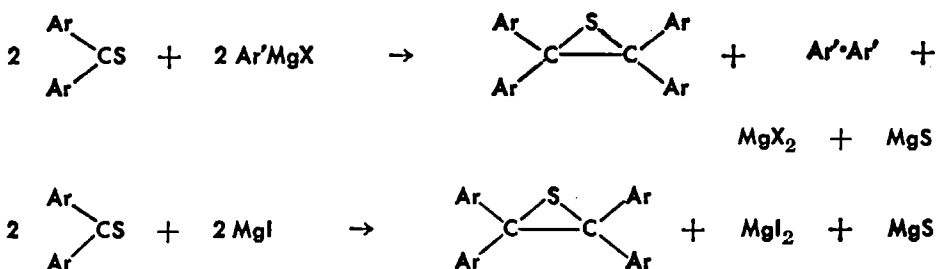
Butyllithium and cyclohexene sulfide give cyclohexene and butyl mercaptan. Grignard reagents act similarly. Lithium aluminum hydride reduces it to the mercaptan.<sup>98</sup>

It is claimed that olefin sulfides can be solvent refined.<sup>204</sup> Ethylene sulfide is said to be stabilized by the addition of hydrogen sulfide or a mercaptan.<sup>166, 510b, 631a</sup> Ethylene sulfide and other cyclic sulfides are reported to be effective insecticides.<sup>346a, 510a</sup> Certain derivatives of ethylene sulfide rank high among insecticides.<sup>237</sup> Polyethylene sulfide may be incorporated with other polymers.<sup>637a</sup>

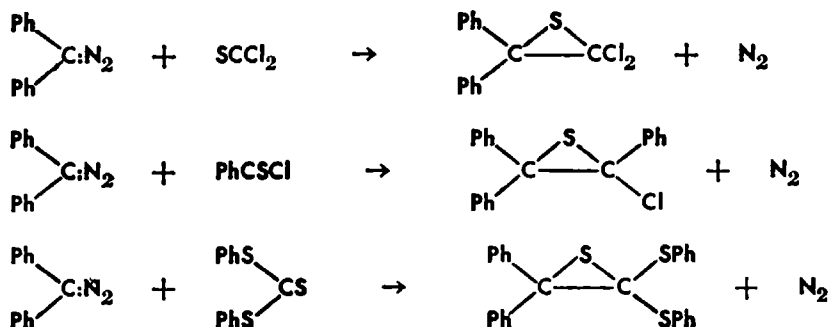
The azeotrope with acetone contains 43% of ethylene sulfide and boils at 51.5°, that with 2,3-dimethylbutane 65%, b. 54°, and that with ethyl formate 53%, b. 50.5°. <sup>402</sup>

### Aromatic Derivatives of Ethylene Sulfide

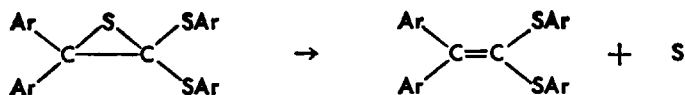
In methods of formation and in reactions, the aromatic derivatives of ethylene sulfide differ radically from the aliphatic. They are formed by the reaction of an aryl Grignard reagent <sup>600</sup> or of magnesium iodide and magnesium <sup>601</sup> on a diaryl thioketone:



Diphenyl diazomethane reacts with thiophosgene, thiobenzoyl chloride,<sup>640b</sup> or diphenyl trithiocarbonate<sup>605a</sup> to give derivatives of ethylene sulfide:

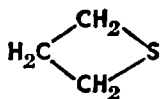


Aromatic derivatives of ethylene sulfide part with their sulfur readily, passing into the corresponding substituted ethylenes. An extreme case is diphenylenedichloroethylene sulfide which loses its sulfur slowly on storage.<sup>640b</sup> From others the sulfur can be removed by copperbronze by heating in solution<sup>599, 605a, 605b</sup> or by nascent hydrogen at room temperature.<sup>600</sup> The mercaptoles of aromatic keto-ketenes were first obtained by desulfurizing the sulfides: <sup>605a</sup>



Attempts to oxidise these cyclic sulfides to the sulfones have failed on account of the lability of the sulfur atom.<sup>640a</sup>

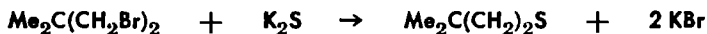
### TRIMETHYLENE SULFIDE



Trimethylene halides and sodium sulfide give the cyclic trimethylene sulfide along with much of the polymer: <sup>75, 101b, 101c, 282a</sup>

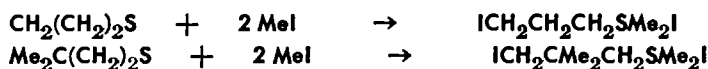


The yield of monomer may be 48%,<sup>75</sup> it is considerably higher when there are alkyls on the central carbon: <sup>30b</sup>



3-Hydroxytrimethylene sulfide,  $S(CH_2)_2CHOH$ , is from sodium sulfide and 1,3-dichlorhydrin<sup>413</sup> or from epichlorhydrin and hydrogen sulfide.<sup>624a</sup> There has been a comprehensive investigation of the thermodynamic properties of trimethylene sulfide.<sup>610</sup>

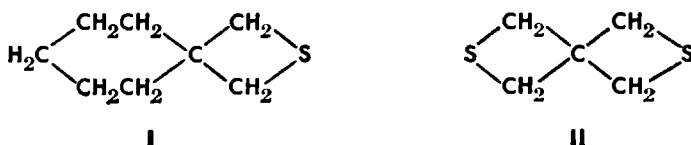
Trimethylene sulfide does not combine with mercuric iodide but does with mercuric chloride to form  $C_3H_6S \cdot HgCl_2$ . It is polymerized by strong acids. It is oxidised to the sulfone by hydrogen peroxide or by permanganate.<sup>101b, 101c</sup> The sulfone can be alkylated in aqueous alkaline solution.<sup>113</sup> The bromine addition compound,  $C_3H_6SBr_2$ , is a solid, unstable at  $-15^\circ$ .<sup>101b, 101c</sup> The ring is opened by treatment with methyl iodide with formation of a sulfonium iodide: <sup>30b, 75</sup>



Trimethylene sulfide, with butyl lithium, gives butyl mercaptan, propyl butyl sulfide, and 1,3-dibutyl mercapto propane,  $BuSCH_2CH_2CH_2SBu$ , while with phenyl lithium it gives 1,6-diphenyl mercapto hexane,  $PhS(CH_2)_6SPh$ , along with phenyl mercaptan and propyl phenyl sulfide.<sup>98</sup>

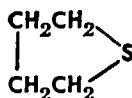
When sodium selenide and trimethylene bromide react a small amount of the monomeric cyclic trimethylene selenide,  $CH_2(CH_2)_2Se$ , is formed along with much of the polymer.<sup>238a, 482c</sup>

Spirosulfides, I and II, are obtained from potassium sulfide with 1,1-bis (bromomethyl)cyclohexane and with pentaerythrityl bromide,  $C(CH_2Br)_4$ :



2-Thia-4-spiro[3.5]nonane (I), boils at  $96^\circ$  at 18 mm. and is oxidised to a sulfone melting at  $73^\circ$ . It combines with 1  $HgCl_2$  m.  $161^\circ$  or 1  $HgBr_2$  m.  $157.5^\circ$ . The methiodide melts at  $92^\circ$ , picrate m.  $117^\circ$ .<sup>34</sup> 2,6-Dithia-4-spiro[3.5]heptane (II), m.  $31.5^\circ$ ,  $b_{16}$   $108-9^\circ$ ,<sup>30a</sup> d 15/4 1.2439,<sup>388</sup> forms a dimethiodide, m.  $144^\circ$ . It can be oxidised to the monosulfoxide, m.  $81.5^\circ$ , the disulfoxide, m.  $146^\circ$ , the sulfoxidesulfone, m.  $156^\circ$ , or the di-sulfone, m.  $244.5^\circ$ . The mono-sulfone, m.  $116.5^\circ$ , can be obtained by the reduction of the sulfoxide-sulfone.<sup>29a, 30a, 388</sup>

## TETRAMETHYLENE SULFIDE, THIOLANE, THIOPHANE

*Formation*

This is frequently called tetrahydrothiophene, though it has seldom been obtained by hydrogenating thiophene. The reverse process, the dehydrogenation of tetramethylene sulfide to thiophene, is not difficult. Thiophane derivatives have become important in connection with biotin. Thiophane chemistry has been reviewed by Wolf and Folkers.<sup>708</sup> Tetramethylene sulfide and its 2-methyl and 3-methyl derivatives have been identified in gasoline.<sup>7, 123, 245, 538</sup>

The formation of this five membered ring is favored; the yield of the sulfide is practically quantitative when a tetramethylene halide is heated with a metal sulfide. The alkyl derivatives are obtained from the corresponding alkyltetramethylene halides.<sup>101c, 106b, 108, 282b, 452</sup>

Tetramethylene glycol, its homologs and analogs are converted to tetramethylene sulfide, or its derivatives, when they are passed with hydrogen sulfide over alumina at around 400°. Tetrahydrofuran may give a 90% yield.<sup>719, 720, 724, 726</sup> Tetramethylene chlorhydrin gives a 95% yield.<sup>720</sup> Alkyltetrahydrofurans give excellent yields of the corresponding alkyltetrahydrothiophenes under similar treatment.<sup>714, 716, 717, 727</sup> The yields of the higher alkylthiophanes are not as satisfactory.

It is possible to hydrogenate thiophene over a platinum catalyst, though it is usually a catalyst poison<sup>454, 455, 456</sup> and can be decomposed by hydrogen over a catalyst.<sup>513</sup> Thiophane can be dehydrogenated over platinum-charcoal.<sup>715</sup> Molybdenum sulfide<sup>149</sup> and palladium-charcoal<sup>496, 497</sup> are satisfactory catalysts for the hydrogenation of thiophene to thiophane. Molybdenum sulfide and other metal sulfides have been studied.<sup>475</sup> 2-Acetylthiophene has been hydrogenated over a cobalt polysulfide catalyst to 2-ethylthiophane.<sup>139</sup> The reduction of thiophene by sodium in alcohol gives 2,3- and 3,4-dihydrothiophenes<sup>82a</sup> which are quite different from the polymeric products from the reaction of 1,4-dibromo-2-butene with sodium sulfide.<sup>626</sup>



The thermodynamic properties of thiophane have been investigated. It melts at  $-96.17^{\circ}$ .<sup>339</sup> Infra red and Raman spectra have been determined for thiophane<sup>227b, 670, 725</sup> and its alpha and beta methyl, ethyl, propyl, and butyl derivatives. An intense line at  $690\text{ cm.}^{-1}$  is apparently characteristic for the thiophane nucleus.<sup>725</sup> The dipole moment of tetrahydrothiophene is 1.87 and that of the selenium compound 1.79.<sup>573a</sup> The rings of these two compounds are not quite planar, a shallow tub form being the most probable.<sup>573b</sup>

Thiophane forms an azeotrope with pyridine boiling at  $113.5^{\circ}$ .<sup>401</sup> Thiophanes can be separated from the aromatic hydrocarbons of approximately the same boiling points by azeotropic distillation. Acetone serves for a thiophane-benzene mixture and methyl ethyl ketone for the methyl derivatives. Other oxygenated compounds may be used.<sup>394</sup> The azeotrope with *trans*-dimethylcyclohexene contains 49% of thiophane and boils at  $115.9^{\circ}$ , that with ethylcyclohexane 84%, b.  $120.5^{\circ}$ , that with 2-methylheptane 44.6%, b.  $114^{\circ}$ , that with 2,5-dimethylheptane 20.7%, b.  $107.9^{\circ}$ , and that with octane 66.3%, b.  $118.4^{\circ}$ .<sup>195</sup>

### Reactions

Thiophane and its alkyl derivatives form complexes with mercuric chloride,  $(\text{CH}_2)_4\text{S}\cdot\text{HgCl}_2$ ,  $(\text{CH}_2\text{CHMe})_2\text{S}\cdot\text{HgCl}_2$ .<sup>7, 123, 245, 282b, 538, 699</sup> Thiophane forms complexes with a wide variety of salts.<sup>502</sup> A study has been made of its identification.<sup>358.5</sup>

Thiophane and chloramine-T give  $(\text{CH}_2)_4\text{S}\cdot\text{NSO}_2\text{C}_6\text{H}_4\text{Me}$ , m.  $135^{\circ}$ , which can also be made from the sulfoxide and *p*-toluenesulfonamide.<sup>659</sup> Chlorination gives  $\delta$ -chlorobutanesulfonyl chloride,  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Cl}$ .<sup>700</sup>

Tetramethylene and pentamethylene sulfides are claimed as flotation agents.<sup>702</sup>

### Substituted Thiophanes

The addition of thioacetic acid to  $\text{Me}_2\text{C}:\text{CH}(\text{CH}_2)_2\text{COMe}$  and hydrolysis of the thioester gives the mercaptan,  $\text{Me}_2\text{CHCH}(\text{SH})\text{CH}_2\text{CH}_2\text{COMe}$ , which can be condensed to 4,5-dihydro-2-methyl-5-isopropylthiophene.<sup>54</sup>

Starting with  $\gamma$ -chlorobutyronitrile and potassium hydrosulfide bis-tetramethylene sulfide has been synthesized.<sup>690</sup> *o*-Xylylene sulfide,  $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{S}$ , its  $\alpha$ -methyl derivative, and its isomer

with the sulfur atom adjacent to the ring have been made.<sup>107, 109</sup>

3,4-Dihydroxythiophane has been obtained from 1,4-dichloro-2,3-dihydroxybutane and sodium sulfide.<sup>384</sup> It may be converted into the 3,4-dichloro- or 3,4-dibromo-thiophane by the action of the halide acids.<sup>371</sup>

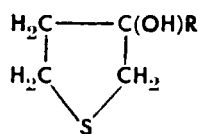
3,4-Diethoxythiophane has been prepared similarly from 2,3-diethoxy-1,4-diiodobutane and potassium sulfide. Treatment with hydrobromic acid converted it to a 3,4-dihydroxythiophane.<sup>528</sup>

A 3,4-diaminothiophane has been prepared from 2,3-diaminobutane-1,4-disulfuric acid and by the degradation of an ester of 3,4-thiophanedicarboxylic acid. Neither product could be converted into the cyclic urea with phosgene.<sup>371, 372</sup> A 3,4-diaminothiophane, which does react with phosgene, has been obtained by the hydrogenation of 2,5-dibromo-3,4-dinitrothiophene with the aid of a palladium catalyst.<sup>495</sup> 3,4-Diaminothiophane and its substitution products will come up again under biotin.

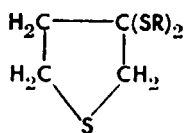
Thiophanone-2 has been made by passing butyrolactone and hydrogen sulfide over alumina at 325–375°. It can be reduced by the Clemmensen method to thiophane but the yield is poor.<sup>728</sup> It is formed in the slow distillation of  $\gamma$ -mercaptobutyric acid.<sup>330</sup> The same thiophanone is obtained when  $\gamma$ -butyrolactone is heated with hydrogen sulfide and a trace of sodium sulfide to 200° for 10 hours.<sup>37</sup>

Thiophanone-3 has been obtained from chloromethyl  $\beta$ -iodoethyl ketone<sup>326, 359</sup> and by the decarboxylation of a 3-ketothiophanecarboxylic acid<sup>364</sup> as will be discussed more fully under biotin. It has been claimed as an antioxidant.<sup>664</sup> This undergoes the typical reactions of a ketone. With methylmagnesium bromide 3-methyl-3-hydroxythiophane, m. 46°, I, is formed. The hydroxyl can be replaced by bromine. Abstraction of hydrobromic acid leaves a 3-methyldihydrothiophene. 3-Phenyl-3-hydroxythiophane has been prepared similarly. Monosodium acetylide puts the ethynyl group,  $-\text{C}:\text{CH}$ , in the 3-position beside the hydroxyl. Mercaptoles, II, are formed in the usual way.<sup>363</sup> Bromination of a thiophanone-3 puts a bromine atom in the 4-position.<sup>362</sup> The methylene group in the 2-position is sufficiently reactive to condense with an aldehyde III.<sup>302, 310, 577</sup>

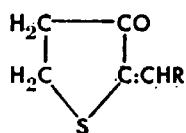
2,5-Diketothiophane,  $(\cdot\text{CH}_2\text{CO})_2\text{S}$ , or succinyl sulfide, has been made from bis-thiolsuccinic acid<sup>694</sup> and by the reaction of succinyl chloride on sodium sulfide.<sup>15a</sup>



I

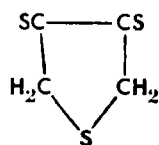


II

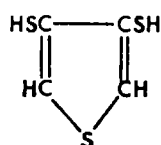


III

Either of the diacetates of 3,4-dimercaptobutanol-1 is converted by sodium bicarbonate to 3-mercaptothiophane.<sup>297</sup> 3,4-Dimercaptothiophane has been reported.<sup>665</sup> One of the by-products in the large scale manufacture of thiophene<sup>130, 550</sup> is a sulfur compound,  $\text{C}_4\text{H}_4\text{S}_3$ , which may be 3,4-thiolanedithione, 3,4-thiophenedithiol or a tautomeric mixture of the two:

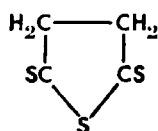
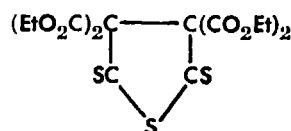


Thiolanedithione



Thiophenedithiol

The dithione structure is favored by the fact that the compound is a vat dye.<sup>129a</sup> An isomer of this is what might be called tri-thiosuccinic anhydride. The tetracarbethoxy derivative of this is formed when bromine is added to sodium malonic ester in carbon disulfide. Analogous compounds are from sodium acetoacetic ester and from sodium cyanoacetic ester.<sup>693</sup>

Trithiosuccinic  
anhydride2,5-Dithiono-3,3,4,4-tetracarbethoxy-  
tetrahydrothiophene

When 2,5-dihydrothiophene is heated with a mercaptan and sulfur, a 3-alkylmercaptothiophane is formed.<sup>82b</sup>

The reduction of 2-thiophenecarboxylic acid by sodium amalgam gives the corresponding tetrahydro acid.<sup>546</sup> 2-Thiophenevaleric acid can be hydrogenated with the aid of a palladium-charcoal catalyst.<sup>497</sup> 2,5-Thiophenedicarboxylic acid can be reduced to the corresponding 2,5-tetrahydrothiophenedicarboxylic acid by zinc in alkaline solution.<sup>216</sup> This same dicarboxylic acid has been obtained from  $\alpha, \alpha'$ -dibromoadipic acid and sodium sulfide.<sup>238c, 672</sup> The DL-acid, which melts at  $166^\circ$ , has been resolved. Both of the active acids melt at  $180^\circ$ , the levo from the brucine

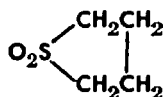
salt has  $[\alpha]/D -225.3^\circ$  and the dextro, from the quinine salt,  $+225.9^\circ$ . The meso-acid melts at  $145^\circ$ .<sup>238c</sup>

Substitution products of thiophane are formed by the addition of chlorine to thiophene.<sup>168, 509</sup> An unstable addition product was noticed as early as 1884.<sup>692</sup> 2,3,4,5-Tetrachlorothiophane can be obtained by chlorinating thiophene below  $-10^\circ$ .<sup>129b, 642</sup> Only two of the possible geometric forms of this have been characterized, the  $\alpha$ - m.  $111.5-113.5^\circ$  and the  $\beta$ - m.  $44.5-6^\circ$ . Two others are believed to exist.<sup>167</sup> The 2,2,3,4,5-pentachlorothiophane is formed by the addition of chlorine to 2-chlorothiophene. The 2,2,3,4,5,5-hexachlorothiophane is obtained similarly from 2,5-dichlorothiophene.<sup>167</sup> A heptachlorothiophane of unknown constitution has been isolated.<sup>170</sup> Chlorination in the presence of much iodine gives octachlorothiophane.<sup>169, 701</sup> In the presence of a catalytic amount of iodine, 2,2,3,4,5,5-hexachlor-3-thiolene is formed.<sup>169</sup>

The addition of sulfur monochloride to 2-methyl- and to 2,3-dimethyl-butadiene gives 3-methyl-3,4-dichlorothiophane and 3,4-dimethyl-3,4-dichlorothiophane, respectively.<sup>33b</sup>

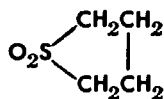
Treating *p*-methoxypropiophenone with phosphorus pentasulfide gives 2,5-di-*p*-methoxyphenyl-3,4-dimethylthiophene.<sup>93b</sup>

### Sulfolane

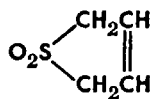


As the sulfur in sulfolane and in sulfolene is not bivalent they do not belong here but they will be mentioned briefly.

Tetramethylene sulfide is oxidised by hydrogen peroxide to the sulfoxide and the sulfone which is known as sulfolane.<sup>659</sup> This contains two hydrogen atoms more than sulfolene, the addition product of sulfur dioxide to butadiene.



Sulfolane



Sulfolene

Sulfolane and its alkyl derivatives can be made by the hydrogenation of the corresponding sulfolenes.<sup>103, 222, 346b, 357, 486</sup>

3,4-Diphenylthiophene sulfone is reduced by zinc and acetic acid to 3,4-diphenylsulfolene which can be hydrogenated with platinum oxide to 3,4-diphenylsulfolane.<sup>28</sup> Sulfolane and sulfo-

lene derivatives may be converted to tetrahydrothiophenes by hydrogen over nickel sulfide.<sup>481</sup>

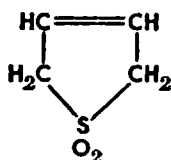
When 3-bromo-3-methyltetrahydrothiophene is oxidised with hydrogen peroxide two sulfones are produced, 3-methylsulfolene and its isomer, having the double bond in the 2,3-position.<sup>360</sup>

Quite a variety of 3,4-derivatives of sulfolene have been obtained by adding chlorine,<sup>488, 490c</sup> bromine,<sup>32, 419</sup> water,<sup>33c, 191, 192, 346c</sup> hydrogen sulfide,<sup>191, 192, 346c</sup> hypochlorous acid,<sup>488, 490b</sup> hypobromous acid,<sup>82</sup> bromotrichloromethane,<sup>368, 369</sup> alcohols,<sup>33c, 47a, 332, 337, 487, 490b, 492</sup> mercaptans,<sup>490e, 491</sup> ammonia,<sup>191, 192, 346c</sup> amines,<sup>191, 192, 346c, 406, 485, 489c, 492</sup> thioacetic acid,<sup>529</sup> or thioglycolic acid<sup>192, 346c</sup> to sulfolene or to its alkyl derivatives. 3-Allyloxysulfolene is recommended as a plasticizer for natural or synthetic rubber.<sup>487</sup> A mercaptan can be added across its double bond.<sup>490d</sup> 2-Vinylsulfolene, from hexatriene, can be hydrogenated to 2-vinylsulfolane or to 2-ethylsulfolane.<sup>483</sup>

The solubility characteristics of sulfolene and of its 3-methyl- and 3,4-dichloro-derivatives have been studied.<sup>357</sup>

Sulfolene is claimed as an aid in the separation of petroleum products from fatty acids and their esters by azeotropic distillation.<sup>489a</sup> It is recommended for the extractive distillation of alcohols<sup>147</sup> and for extracting sulfur dioxide.<sup>333</sup> Sulfolanes may be stabilized with tertiary amines.<sup>489b</sup> Some of the sulfolanes are said to be useful as selective solvents<sup>220, 636</sup> and as oil additives.<sup>490a</sup> The alkoxy derivatives are claimed to be plasticizers for cellulose ethers<sup>332</sup> and the 3-methoxy- and 3-methylamino- for polyvinyl alcohol.<sup>492</sup> Derivatives with unsaturated side-chains may be polymerized.<sup>621</sup>

### Sulfolene



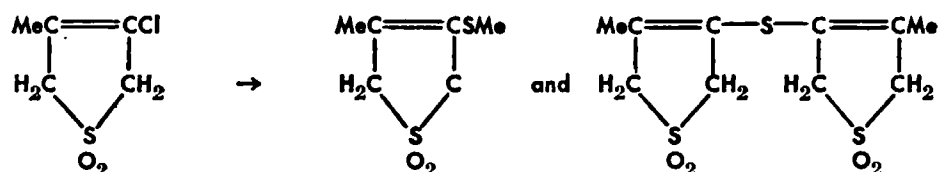
The literature on this class is extensive and no attempt will be made to cover it.

Sulfolene, or butadiene sulfone, is made by the addition of sulfur dioxide to butadiene; homologs and derivatives are from the same reaction with hydrocarbons and their derivatives that have

conjugated double bonds.<sup>26, 484</sup> The formation of a sulfolene may serve to isolate a diolefin from a mixture of hydrocarbons.<sup>572, 637b</sup> Specific reaction rates for formation and decomposition of sulfolene have been measured.<sup>202</sup> The bond lengths in  $\beta$ -isoprene sulfone are: C—C for the ring 1.41 Å, C—S 1.75 Å, and S—O 1.44 Å.<sup>171</sup> These have been reinterpreted.<sup>375</sup>

The addition of various substituents to sulfolene to form sulfolane derivatives has been mentioned above.

The addition of sulfur dioxide to 2-methyl-3-chlorobutadiene gives a 3-chlorosulfolene which reacts with potassium mercaptide or sulfide:<sup>25, 26</sup>



Both of these sulfides can be oxidised to sulfones.<sup>25</sup>

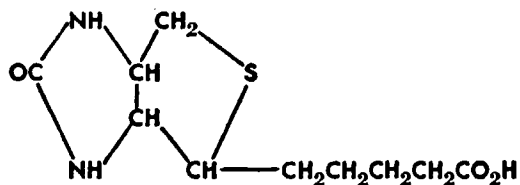
Selenious acid reacts with dienes to form analogous compounds.<sup>33a</sup>

#### *Tetramethylene Selenide and Telluride*

Tetramethylene selenide has been prepared from tetramethylene bromide and sodium selenide.<sup>482a</sup> Exhaustive chlorination of selenophene gives 2,2,3,4,5,5-hexachloroselenolane. Chlorination at  $-15^\circ$  in carbon disulfide yields 2,3,4,5-tetrachloroselenolane. Bromination under the same conditions leads to a hexabromo-compound.<sup>652</sup> The 2,5-dicarboxylic acid has been prepared and resolved.<sup>238b</sup>

Tetramethylene telluride,  $(\cdot\text{CH}_2\text{CH}_2)_2\text{Te}$ , has been prepared from tetramethylene bromide and sodium telluride.<sup>224</sup> It had been obtained previously by removing iodine from the iodide,  $(\cdot\text{CH}_2\text{CH}_2)_2\text{TeI}_2$ , which is formed when tetramethylene iodide is heated with amorphous tellurium.<sup>482e</sup>

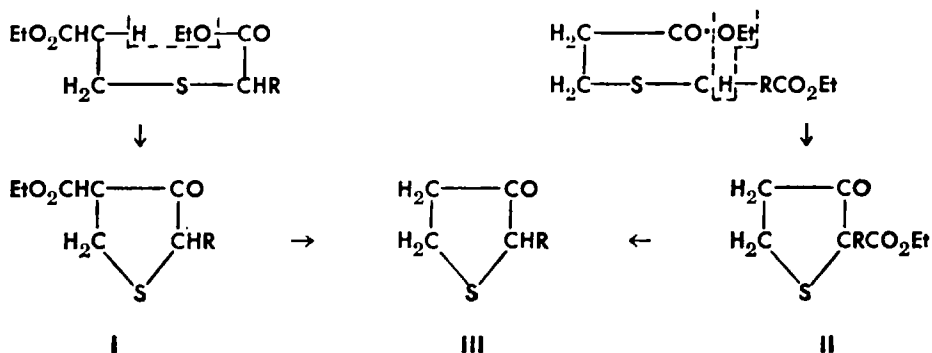
#### *Biotin*



The elucidation of the structure of this important growth factor<sup>122, 128, 211, 328, 377, 378, 379, 380, 381, 461, 462, 463, 677, 678, 679, 680, 703</sup> started a number of investigations looking toward its synthesis.<sup>43, 44, 155, 268, 283, 309, 590</sup> As appears in the formula above, biotin consists of a thiophane and a diazolidine ring fused together. Obviously it should be formed by the reaction of phosgene on 2-(4-carboxybutyl)-3,4-diaminothiophane. This has proved to be true but the synthesis of the right stereoisomer of the intermediate has been far from easy. It has, however, been accomplished in several ingenious ways.

The first undertaking was to synthesize what might be called norbiotin, that is biotin without the valeric acid side chain. This requires 3,4-diaminothiophane as the critical intermediate. As there is no known way of introducing amino groups directly, the thiophane ring must be put together with groups in the 3 and 4 positions which can be transformed into amino, with the proper configurations. The various syntheses of biotin differ from each other chiefly in the choice of these two groups and in the means devised for changing them into amino. When a synthesis of norbiotin has been worked out the final step is to repeat it using intermediates containing the  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$  side chain, or a group which may be changed into this, properly placed. As a preliminary to this, syntheses have been carried through with simpler groups such as methyl<sup>125, 364, 586</sup> or phenyl.<sup>586, 654</sup>

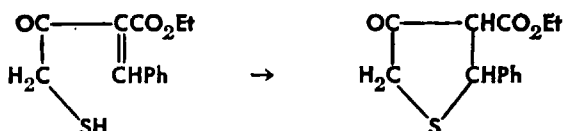
The first step in a number of syntheses is the Dieckmann self-condensation of a sulfide ester<sup>478, 708</sup> such as  $\text{EtO}_2\text{CCH}_2\text{CH}_2\text{SCHRCO}_2\text{Et}$ .<sup>480</sup> This may take place in either one of two ways: 22, 38, 118, 119, 125, 155, 326, 364, 395c, 575, 585



With sodium methylate in toluene at  $80^\circ$  I is formed while in ether at room temperature II is the chief product.<sup>712</sup> The con-

condensation takes place rapidly in methanol or ethanol as solvents to give II.<sup>477</sup> The formation of I rather than II seems to be favored when R is a bulky group. The substituent may be in the other end of the sulfide ester as in  $\text{EtO}_2\text{CCH}_2\text{CHRSCH}_2\text{CO}_2\text{Et}$ . The cyclization of this puts the R on the other side of the ring in I, adjacent to the ester group instead of next to the carbonyl.<sup>396</sup> This makes no difference in the final product. Both I and II have the aceto-acetic ester structure and may be saponified and decarboxylated to the thiophanone, III.

The reaction of  $\alpha$ -benzylidene-  $\gamma$ -chloroaceto-acetic ester with sodium hydrosulfide gives 2-phenyl-3-carbethoxythiophanone-4. The mercaptoacid, which must be the primary product, adds to itself across the double bond:<sup>654</sup>



Very similar to this is the self-condensation of  $\alpha$ -cyano- $\gamma$ -mercaptoacetoacetic ester to 2-imino-3-carbethoxy-4-keto-thiophane.<sup>68</sup>

Some of the ways in which amino groups can be gotten into positions 3 and 4 are sketched. For details the original references must be consulted.

The problem of converting the keto group of the thiophanone-3 into an amino has been solved in several ways. One frequently used is to make the oxime<sup>156, 299, 300, 305, 308, 364, 584</sup> or hydrazone<sup>300</sup> which can be reduced.<sup>495</sup> The amino group thus formed may be acetylated to protect it during subsequent operations.<sup>300, 301, 310, 364</sup> A peculiar reduction of the oxime takes place when it is treated with hydrogen chloride in ether solution. The product is the corresponding aminothiophene, the required hydrogen coming from the thiophane ring.<sup>155</sup> This is one step in the synthesis of tetrahydrobiotin which can be hydrogenated to DL-biotin with the aid of a molybdenum sulfide catalyst.<sup>154</sup> The dehydration of a hydroxyimidazolidothiophane with sulfuric acid in methanol gives an alkylidene compound which may be hydrogenated.<sup>653</sup>

The thiophanone may be converted to the cyanhydrin by hydrocyanic acid.<sup>38</sup> This can be dehydrated and the unsaturated

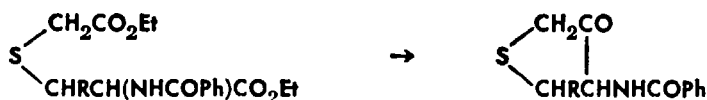


nitrile hydrogenated and esterified.<sup>42, 118, 326, 590, 591, 654</sup> Or the hydroxyl may be replaced by a chlorine which is then removed by zinc leaving the  $-\text{CN}$  group which is changed to  $-\text{CO}_2\text{Et}$ .<sup>285</sup>

The ester group may be converted to the amino by the Curtius degradation:  $-\text{CO}_2\text{Et} \rightarrow -\text{CONHNH}_2 \rightarrow -\text{CON}_3 \rightarrow -\text{NHCOOEt} \rightarrow -\text{NH}_2$ <sup>45, 120, 155</sup> This may be done for either one or two such groups.<sup>44, 120, 574</sup>

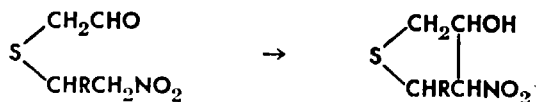
The  $-\text{CO}_2\text{Et}$  group in position 4 may be eliminated and the resulting thiophanone brominated. The bromine is replaced by hydroxyl and the 4-hydroxythiophanone-3 treated with an excess of hydroxylamine to give the 3,4-dioxime which is reduced to the diamino.<sup>361, 362</sup>

Another approach has been the self-condensation of a benzamido derivative of the sulfide ester: <sup>42, 299, 302, 303, 304, 309, 310, 578, 709, 711</sup>



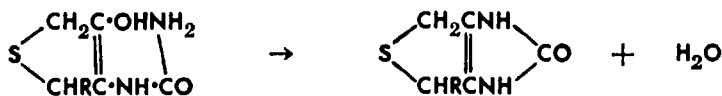
This has been carried out on the unsubstituted ester and with  $\text{R} = -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ . It has the advantage that one potential amino group is already in place.

Cyclization of a sulfide containing nitro and aldehyde groups has been effected: <sup>283, 294</sup>



This has been carried out with  $\text{R} = \text{Me}$  and with  $\text{R} = -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ . The nitro group is easily reduced and the hydroxyl can be changed to the amino.<sup>495</sup> The acetal,  $(\text{EtO})_2\text{CHCH}_2\text{SCHRCH}_2\text{NO}_2$ , can be substituted for the aldehyde in this condensation.<sup>283, 294, 521</sup>

In one synthesis the 3-aminothiophanone-4 was treated with a metal cyanate and the resulting urea condensed. The thiophanone is written in the enol form: <sup>578</sup>

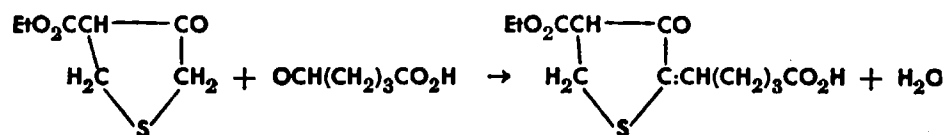


The last step, closing the urea ring by treating the 3,4-diaminothiophane with phosgene goes easily.<sup>44, 121, 155</sup>

Quite a different synthesis of biotin starts with 1,2-dibenzylaminosuccinic acid which is converted to the urea by phosgene. By a series of reactions the succinic acid part is made into a thiophanone-2 and the side chain attached by the Grignard reaction. Finally the benzyl groups are removed. A meso-diaminosuccinic acid derivative, as a starting material, is claimed in a series of patents.<sup>276, 277</sup>

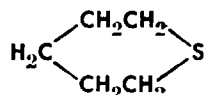
Another synthesis depends on the reaction of ureidothiophane-carbohydrazides with nitrous acid and an acidic catalyst which leads to rearrangement of the hydrazide to an amine and the formation of an imidazolidothiophane ring.<sup>41, 121</sup>

The valeric acid side-chain may be put on after the condensation to the thiophanone has been effected. Thus 2-carbethoxythiophanone-3, which has the characteristic structure of an acetoacetic ester, is treated with sodium ethylate and 3-iodopropylmalonic ester,  $\text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$ .<sup>23, 575</sup> Another way of doing this is to condense an aldehydoacid,  $\text{OCH}(\text{CH}_2)_n\text{CO}_2\text{H}$ , with the  $=\text{CH}_2$  in position 2 of a thiophanone-3.<sup>302, 310, 577</sup>



Considerable attention has been given to the stereoisomerism of biotin and related compounds particularly the 3,4-thiophane-dicarboxylic acid and its derivatives.<sup>39, 40, 43, 45, 119, 234, 306, 307</sup> DL-Biotin has been resolved by combining it with arginine<sup>235</sup> and by causing its acid chloride to react with mandelic acid.<sup>710</sup>

#### PENTAMETHYLENE SULFIDE



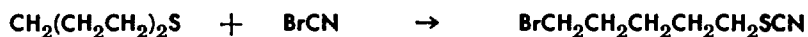
This has been made by treating pentamethylene halides with alkali sulfide.<sup>101c, 106a, 106b, 108, 159, 282c, 504a</sup> As has been mentioned earlier in this chapter, the yields are much lower than with the tetramethylene halides.

Pentamethylene oxide is converted to the sulfide by passing over alumina with hydrogen sulfide.<sup>723</sup> The cyclic sulfide is formed, with the unsaturated sulfide, when tetrahydrofurfuryl alcohol is subjected to the same treatment.<sup>504c</sup> Its 2-methyl-, 2,2-dimethyl-, 2,2,6,6-tetramethyl-, and 2,2,6-trimethyl-6-ethyl- derivatives have been obtained from the corresponding oxides and phosphorus pentasulfide.<sup>504a</sup> The last two compounds have been made by adding hydrogen sulfide to geraniolene<sup>619</sup> and dihydromyrcene, respectively.<sup>504b, 619</sup> From *o*-amino-3-chloropropylbenzene a cyclic sulfide has been prepared by means of the diazo reaction.<sup>108b</sup>

The Raman spectra of pentamethylene sulfide,<sup>229b</sup> cyclohexanone and piperidine have been compared.<sup>681</sup> The infrared<sup>618</sup> and general light absorption<sup>336</sup> have been studied. The ultraviolet absorption of its 4-keto derivative has been determined.<sup>227b</sup> Pentamethylene sulfide forms a colored addition compound with tetranitromethane.<sup>681</sup> The vapor pressure-temperature relationship has been worked out.<sup>698</sup>

Mercuric chloride addition products of pentamethylene sulfide and of its methyl derivative are known.<sup>101a, 101c, 282c</sup> The mercuric iodide and bromine addition compounds are unstable. The sulfone is obtained by oxidation with permanganate or with hydrogen peroxide.<sup>101a, 101c</sup> Treating the methyl iodide addition product with alkali gives the sulfonium hydroxide,  $\text{CH}_2(\text{CH}_2\text{CH}_2)_2\text{SMeOH}$ . When this is pyrolyzed the pentamethylene sulfide is regenerated. When  $\alpha$ -methylpentamethylene sulfide is subjected to the same treatment the ring is ruptured and an unsaturated sulfide,  $\text{MeCH:CHCH}_2\text{CH}_2\text{CH}_2\text{SMe}$ , is formed.  $\alpha$ -Methyl-tetrahydrothiophene behaves in the same way giving the sulfide,  $\text{MeCH:CHCH}_2\text{CH}_2\text{SMe}$ .<sup>282e</sup>

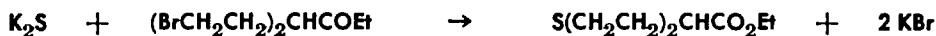
Pentamethylene sulfide is opened up by cyanogen bromide:<sup>108</sup>



A sulfonium compound is probably the intermediate.

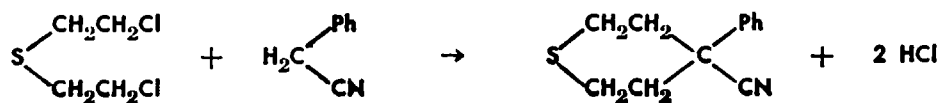
A number of alkylated cyclic sulfides have been isolated from Naft-Khaneh distillate. Among these are 2,3- and 2,4-dimethyl-, 2-ethyl- and 2,3,5-trimethyl-cyclothiapentanes and 2-, 3- and 4-methyl- and 2,6- and 3,4-dimethyl-cyclothiahexanes.<sup>81</sup>

Ethyl pentamethylene sulfide-carboxylate has been prepared:



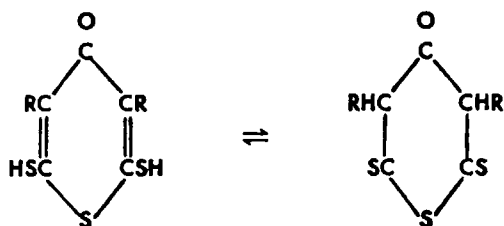
The ester has been reduced to the alcohol,  $S(CH_2CH_2)_2CHCH_2OH$ .<sup>541</sup> The ethyl ester,  $S(CH_2CH_2)_2CHCH_2CO_2Et$ , has been made similarly and reduced to the alcohol,  $S(CH_2CH_2)_2CHCH_2CH_2OH$ .<sup>542</sup> The *cis* 2,6-dicarboxylic acid has been made from  $\alpha,\alpha'$ -dibromopimelic acid.<sup>228, 607d</sup>

4-Phenyl-4-cyanopentamethylene sulfide has been obtained by alkylating phenylacetonitrile with  $\beta,\beta'$ -dichloroethyl sulfide: <sup>207, 208, 209, 346d</sup>



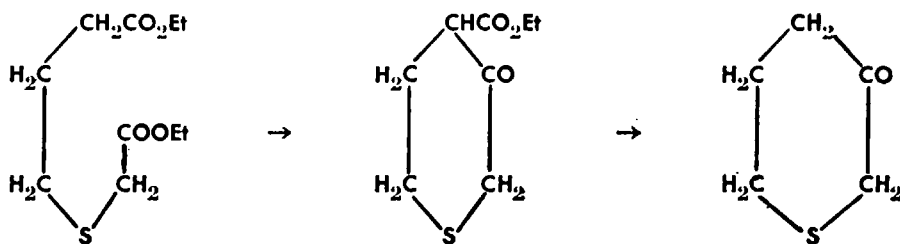
By a series of reactions 4-ketopentamethylene sulfide,  $S(CH_2CH_2)_2CO$ , has been prepared from  $\beta$ -sulfidopropionic ester,  $S(CH_2CH_2CO_2Et)_2$ . The phenylhydrazone can be condensed to penthienoindole, m.  $157^\circ$ . When 4-hydroxy-4-carboxypenthiene, or the 4-hydroxy-4-phenyl-, or 4-hydroxy-4-benzyl- derivatives are oxidised to the sulfoxide *cis* and *trans* isomers, which can be separated by crystallization, are produced.<sup>76, 78, 146, 227a</sup> A mercaptone,  $S(CH_2CH_2)_2C(SET)_2$ , is formed from this as well as from its 2-methyl- and 2,6-dimethyl derivatives.<sup>52</sup> The alkyl derivatives are from the corresponding substituted sulfidopropionic esters.<sup>53</sup>

There seems to be tautomerism between 2,6-dimercaptopyrone and 2,6-dithiono-4-ketopentamethylene sulfide: <sup>594</sup>



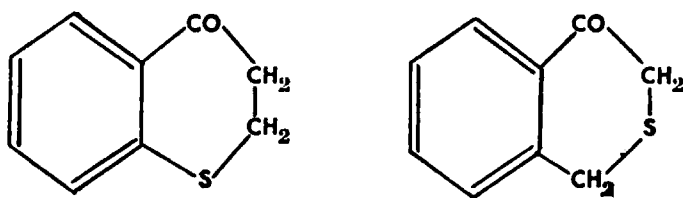
By the addition of hydrogen sulfide to the unsaturated ketones,  $H_2C:CHCOCH_2CH:CH_2$ ,  $H_2C:CMeCOCH_2CH:CH_2$ ,  $EtCH:-CPrCOCH_2CH:CH_2$ ,<sup>505a</sup> and  $Me_2C:CHCOCH:CMe_2$ ,<sup>504c</sup> the 2-methyl-, 2,5-dimethyl-, 2-methyl-5-propyl-6-ethyl-, and the 2,2,5,5-tetramethyl-derivatives are obtained. Acetylene can be added to the carbonyl to give the 4-ethynyl-4-hydroxy compounds.<sup>505b</sup>

The isomeric 3-ketopentamethylene sulfide is obtained by saponification and decarboxylation of the self-condensation product from a sulfide ester: <sup>228, 408</sup>



$\delta$ -Thiovalerolactone may be called 2-ketopentamethylene sulfide.<sup>37, 583</sup>

The two acids  $\text{PhSCH}_2\text{CH}_2\text{CO}_2\text{H}$  and  $\text{PhCH}_2\text{SCH}_2\text{CO}_2\text{H}$  can be condensed to thiatetralones:<sup>370</sup>



$\gamma$ -Thiopyron,  $\text{S}(\text{CH}:\text{CH})_2\text{CO}$ , can be made from penthione,  $\text{S}(\text{CH}_2\text{CH}_2)_2\text{CO}$ , by treatment with phosphorus pentachloride. The 2,6-dimethylmercapto-1-thiopyrone,  $\text{S}(\text{CSMe}:\text{CH})_2\text{CO}$ , has been prepared by decarboxylating the 3,5-dicarboxy acid.<sup>13</sup> By the reaction of a ketone with potassium hydroxide and carbon disulfide, followed by potassium sulfide, 2,6-dimercapto-3,5-dialkyl-1-thiopyrones,  $\text{S}[\text{C}(\text{SH}):\text{CR}]_2\text{CO}$ , are obtained.<sup>8, 9, 10</sup> Ethyl ketoglutarate,  $\text{OC}(\text{CH}_2\text{CO}_2\text{Et})_2$ , acetaldehyde, and hydrogen sulfide, with piperidine, give 2,6-dimethyl-3,5-dicarbethoxy-penthione.<sup>334</sup> Phorone and hydrogen sulfide, with an alkaline catalyst, unit to form 2,2,6,6-tetramethyl-1-4-penthione which can be reduced to the tetramethylcyclopentamethylene sulfide.<sup>14</sup>

Thiophene has been prepared from sodium succinate and phosphorus pentasulfide.<sup>682</sup> This method has been applied to sodium

$\alpha$ -methyl-glutarate. The product is  $\text{S}$   $\text{CH}_2$ . The yield

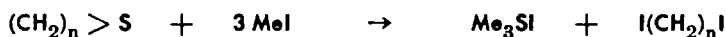
was only 12% while it is around 50% in the thiophene synthesis. This unsaturated compound, methylpenthiothiophene, resembles thiophene in its ease of acetylation.<sup>390</sup>

Pentamethylene selenide has been prepared from pentamethyl-

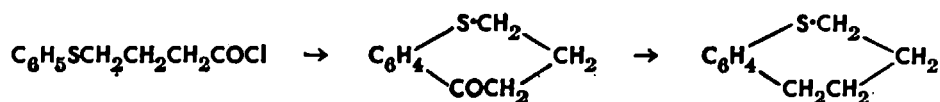
ene bromide and sodium selenide.<sup>482b</sup> A tellurium analog has been described.<sup>224</sup>

### LARGER RINGS

Hexamethylene sulfide,  $(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$ , has been obtained, in poor yields, from hexamethylene halides and metal sulfides.<sup>106b, 282d</sup> By adding a polymethylene bromide and sodium sulfide, a little at a time to a large volume of boiling alcohol, several higher members of the series,  $(\text{CH}_2)_{12}\text{S}$ ,  $(\text{CH}_2)_{13}\text{S}$ , and  $(\text{CH}_2)_{14}\text{S}$ , have been prepared. The tetradecamethylene sulfide has a distinct, though faint, musk odor. These cyclic sulfides combine with methyl iodide to form  $(\text{CH}_2)_n > \text{SMeI}$  but with an excess of methyl iodide the ring is opened: <sup>498</sup>



By condensing  $\gamma$ -phenylmercaptobutyryl chloride with itself and reducing the ketone a bicyclic sulfide has been obtained: <sup>131</sup>

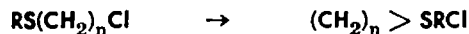


An isomer of this has been obtained from *o*-(3-bromopropyl) benzyl bromide and sodium sulfide.<sup>107</sup> Other bicyclic sulfides have been separated from petroleum fractions, 1-thiaindane, 2-thiaindane, 1-thiatetralin, *cis*-3-thia[0,3,4]bicyclononane, and *trans*-2-thia[0,4,4]bicyclodecane.<sup>81</sup>

Hexamethylene selenide,  $(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{Se}$ , is analogous to hexamethylene sulfide in its formation, properties, and reactions. It forms a dichloride, a dibromide, and a diiodide.<sup>482d</sup>

### CYCLIC SULFONIUM COMPOUNDS

Extensive studies have been made of ring closure with sulfide-halides,  $\text{RS}(\text{CH}_2)_n\text{Cl}$ :

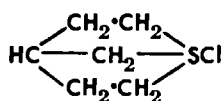


The tetramethylene compound  $\text{EtS}(\text{CH}_2)_4\text{Cl}$ , changes to the sulfonium chloride on standing. The relative rates of formation of five, six, and seven membered rings are 6000:76:1. Rings of 8 to 13 members do not appear to be formed.<sup>69b, 73, 74, 77</sup>

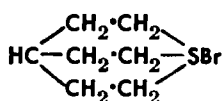
By heating several of these compounds with sodium iodide in acetophenone until no more methyl iodide is evolved, tetra-

decamethylene sulfide,  $(\text{CH}_2)_{14}\text{S}$ , hexadecamethylene sulfide,  $(\text{CH}_2)_{16}\text{S}$ , and octadecamethylene sulfide,  $(\text{CH}_2)_{18}\text{S}$ , were obtained.<sup>73</sup>

4-Chloromethylpentamethylene sulfide<sup>541</sup> and 4-bromoethylpentamethylene sulfide<sup>542</sup> condense to the bicyclic sulfonium compounds I and II, respectively:



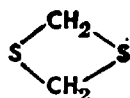
I



II

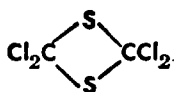
### Rings Containing Two Sulfur Atoms

#### TWO SULFUR AND TWO CARBON ATOMS

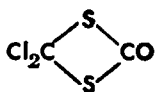


The simple cyclic compound here represented has not been prepared but what appear to be its derivatives are known.

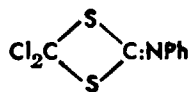
The dimer of thiophosgene (I), the ketone obtained by replacing two of its chlorine atoms by oxygen (II), and the reaction product with aniline (III) have been given these structures: 190, 603



I



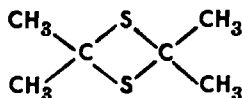
II



III

Thiophosgene dimer was formerly assigned a linear structure,  $\text{Cl}_3\text{CSCSCl}$ .<sup>551</sup> The melting points are suspiciously high for monomers.

By heating acetone and phosphorus pentasulfide a compound was obtained having the composition and molecular weight corresponding to the formula,  $(\text{C}_3\text{H}_6\text{S})_2$ . This was called "duplo-sulfacetone" and assigned the cyclic formula: 16, 393, 635b, 704



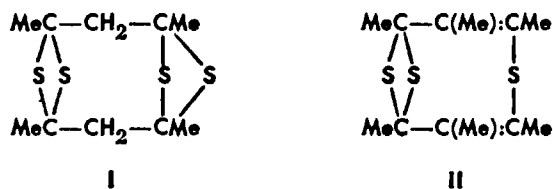
The same compound was formed when acetone and phosphorus trisulfide were heated together in a sealed tube. Doubt has been

cast on this compound.<sup>89</sup> What was supposed to be the same compound was obtained by the oxidation of *i*-propyl mercaptan.<sup>161b</sup> The disulfone is stable.<sup>16</sup> A compound which may be of this type has been prepared by treating acetophenone with hydrogen sulfide and hydrogen chloride.<sup>137</sup>

By heating ketones with phosphorus pentasulfide several dimeric thioketones have been obtained:  $(\text{Me}_2\text{CS})_2$ ,  $(\text{MeCSEt})_2$ , and  $(\text{Et}_2\text{CS})_2$ . The product from dipropyl ketone was a mixture of monomer and dimer.<sup>392</sup> Benzylideneacetone, ammonia, and hydrogen sulfide give the dimer,  $\text{PhCH:CHC}(\text{Me})(\text{S})_2\text{C}(\text{Me})\text{CH:CHPh}$ .<sup>249</sup> A compound of this type related to benzaldehyde has been reported.<sup>61</sup>

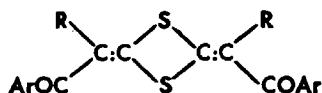
Materials obtained by heating unsaturated ketones with phosphorus pentasulfide have been claimed as oil additives.<sup>514, 555</sup>

Treating acetylacetone with hydrogen sulfide and hydrochloric acid<sup>409</sup> gives a compound, melting at  $161^\circ$ , to which has been assigned structure I. From 3-methylacetylacetone with the same reagents a product, II, melting at  $193^\circ$  and containing only three atoms of sulfur was obtained:



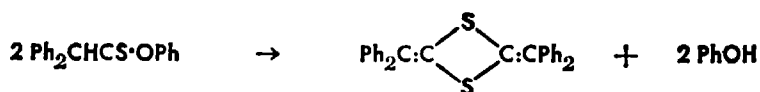
3,3-Dimethylacetylacetone gives a tetramethyl derivative, m.  $227^\circ$ , corresponding to I while 3-methylacetylacetone gives two compounds of the same composition.<sup>256</sup> Quite different structures have been suggested for these dithioderivatives of  $\beta$ -diketones.<sup>240</sup> Complicated compounds have been obtained from benzoin by similar treatment.<sup>470b</sup>

The desaurines may be placed here since they are believed to have the structure: <sup>79, 366b, 465b, 467</sup>

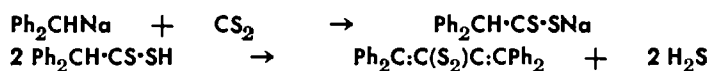


The dimeric diphenyl thioketene is a yellow, stable, slightly soluble, high melting compound formed when phenyl diphenylthionacetate, or dithio-acetate, is heated to  $280^\circ$ :<sup>608</sup>





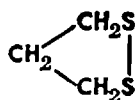
The same compound may be obtained by treating diphenylmethyl sodium with carbon disulfide, acidifying and heating:<sup>604</sup>



Somewhat analogous compounds,  $\text{Me}_2\text{CSe}_2\text{CMe}_2$ ,  $\text{Me}_2\text{CSe}_2\text{CEt}_2$ , and  $\text{Me}_2\text{CSe}_2\text{CPh}_2$ , are from the ketones and hydrogen selenide in the presence of hydrochloric acid.<sup>432</sup>

### THREE CARBON AND TWO SULFUR ATOMS

#### Trimethylene Disulfide



This is the only important group of the cyclic disulfides. Trimethylene disulfide and some of the higher ones have been obtained by the steam distillation of the appropriate Bunte salts. As appears in Table 4.1 the yields vary greatly with the size of the ring.

TABLE 4.1

*Yields and Relative Activities of Cyclic Disulfides —S—R—S—*

No. Members		Yield	Activity
4	—(CH <sub>2</sub> ) <sub>2</sub> —	trace	6
5	—(CH <sub>2</sub> ) <sub>3</sub> —	60%	5+
6	—(CH <sub>2</sub> ) <sub>4</sub> —	22	5
7	—(CH <sub>2</sub> ) <sub>5</sub> —	13	1
8	—(CH <sub>2</sub> ) <sub>6</sub> —	4	5
9	—(CH <sub>2</sub> ) <sub>7</sub> —	2	1
10	—(CH <sub>2</sub> ) <sub>8</sub> —	3	5
11	—(CH <sub>2</sub> ) <sub>9</sub> —	0.2	1
12	—(CH <sub>2</sub> ) <sub>10</sub> —	2	5+
7	—(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> —	50	4
9	—(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> —	1	1

The monomers pass over as oils which soon polymerize, some more rapidly than others. Figures for the relative rates are in the table under "Activity." On this account it is not practicable to determine physical properties of the monomers.<sup>2</sup> It is to be noted that there is no relation between the stabilities of the various rings and the amounts of them that are formed. The yield of any ring depends on the probability of the two sulfur atoms being close together at the time the Bunte salt is broken apart. The yield of the trimethylene disulfide is high but it is unstable, while the eleven membered ring is relatively stable though the yield is small. These cyclic disulfides tend to go into linear polymers.<sup>351, 669</sup>

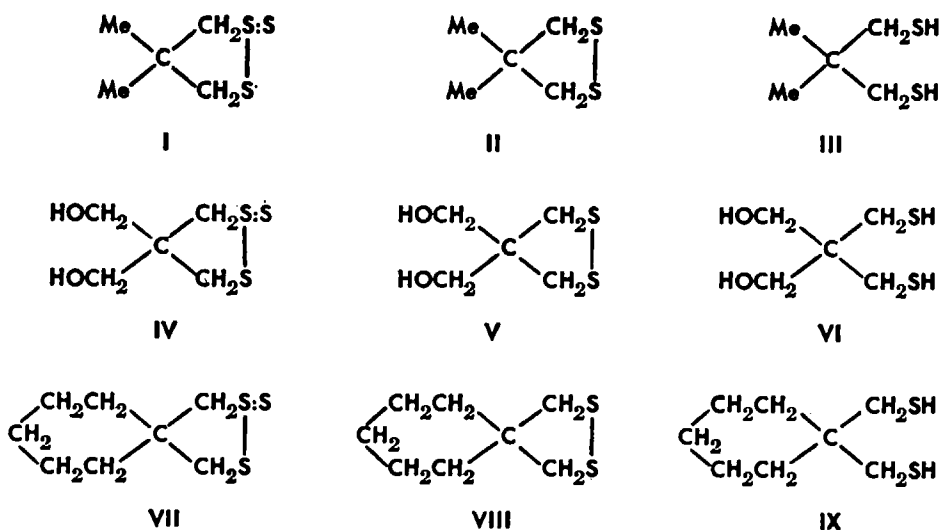
A compound having the composition of trimethylene disulfide was obtained by treating trimethylene thiocyanate with potassium hydroxide and also by oxidising trimethylene dimercaptan, but the melting points given, 71° and 75°, and the low solubility in organic solvents are proof of its polymeric nature.<sup>20a, 295</sup> Some of this is formed when trimethylene sulfide is passed over alumina at 250°. It can be reduced to trimethylene mercaptan by zinc and acid.<sup>718</sup> Recently it has been found that the monomeric trimethylene disulfide can be obtained by the steam distillation of the polymer in the presence of sodium hydroxide and polysulfide<sup>53.7</sup> or of the trimethylene Bunte salt with cupric chloride.<sup>2</sup> This ring is of particular interest since it is the distinctive part of lipoic acid which will be considered in a later section. Its absorption spectra have been studied from that point of view.<sup>136.5</sup>

Trimethylene disulfide is said to improve the film strength of lubricating oils.<sup>415b</sup>

The reaction of sulfur chloride with naphthalene has been supposed to give a cyclic disulfide, 1,3-C<sub>10</sub>H<sub>6</sub>S<sub>2</sub>, which would be of this type.<sup>620</sup>

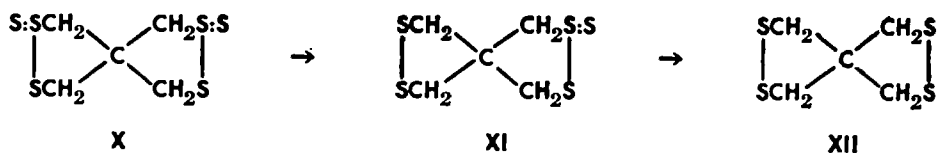
Trimethylene disulfide rings that contain substituents are much more stable. Dimethyl-, bis (hydroxymethyl)-, and pentamethylene derivatives have been prepared from the corresponding dibromides, Me<sub>2</sub>C(CH<sub>2</sub>Br)<sub>2</sub>, (HOCH<sub>2</sub>)<sub>2</sub>C(CH<sub>2</sub>Br)<sub>2</sub>, and C<sub>5</sub>H<sub>10</sub>C(CH<sub>2</sub>Br)<sub>2</sub>, with potassium disulfide or tetrasulfide. The use of the tetrasulfide avoids contamination with the monosulfide. The immediate products are trisulfides, I, IV and VII, from which one third of the sulfur can be removed by copper powder. Reduction

converts the disulfides, II, V, and VIII to the dimercaptans, III, VI, and IX.



The structures given for I, IV, and VII are in accordance with the easy removal of one third of the sulfur. The oxidation of the disulfides gives disulfonic acids. The dimercaptans react with aldehydes and ketones to form 1,3-dithianes which will be considered later.<sup>34</sup>

Pentaerythrityl bromide,  $C(CH_2Br)_4$ , reacts with potassium tetrasulfide to give a product which melts at  $184^\circ$  and has the composition,  $S_3(CH_2)_2C(CH_2)_2S_3$ . Boiling this with potassium sulfide in alcohol removes one atom of sulfur and boiling with copper in toluene takes off another. The desulfurization has been represented thus:



Oxidation of any one of these leads to the tetrasulfonic acid,  $C(CH_2SO_3H)_4$ . Treatment of XII with sodium gives the sodium derivative of the mercaptan  $C(CH_2SH)_4$ . This reacts with two molecules of an aldehyde or a ketone to give double mercaptals or mercaptoles. These are 1,3-dithianes and will be taken up in a later section.

When potassium disulfide is used instead of the tetrasulfide, the product, XIII, m.  $78.5^\circ$ , has the same composition as XII

but has different properties. One of its four sulfur atoms is removed by copper to  $C_5H_8S_3$ , m.  $56.5^\circ$ , and oxidation gives a sulfone-disulfonic acid. Two structures, XIII and XIV have been proposed.

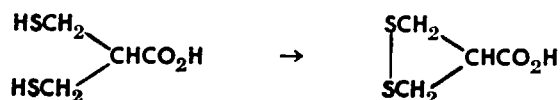


Either of these would account for the easy removal of one fourth of the sulfur and for the oxidation to a sulfone-disulfonic acid.<sup>29a, 29b, 29c</sup> Structure XIII is improbable as there is no authenticated case on record of a disulfide of the structure  $R_2S:S$  while it is well known that a disulfide,  $RS\cdot SR$ , does take up sulfur, the removal of which regenerates the disulfide:

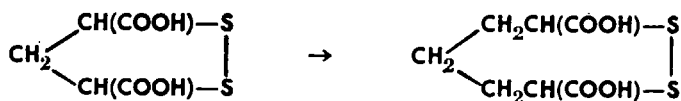


The structure of the trisulfide group, which has evoked much discussion, will be taken up in Chapter 7.

Oxidation of  $\beta,\beta'$ -dimercapto-*i*-butyric acid gives the disulfide-acid:



This has been isolated from asparagus.<sup>352</sup> Dicarboxy derivatives of cyclic disulfides:



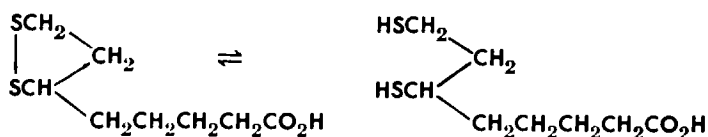
have been obtained from  $\alpha,\alpha'$ -bromoglutaric and  $\alpha,\alpha'$ -dibromopimelic acids.<sup>607a</sup> Treating 1,3-dimercaptoacetone with iodine is supposed to give the ketodisulfide,  $OC(CH_2S\cdot)_2$ , but this has not been well characterized.<sup>607c</sup>

### $\alpha$ -Lipoic Acid

$\alpha$ -Lipoic acid, only recently discovered, has been found to be an important factor in photosynthesis,<sup>136a</sup> in pyruvic acid oxidation,<sup>290, 511, 547, 557a, 611a, 628</sup> and in growth.<sup>557b, 611b, 625</sup> It appears to aid the functioning of certain enzymes.<sup>557c, 611c</sup> A mechanism

for its action has been proposed.<sup>557c</sup> At first  $\alpha$ -lipoic acid was supposed to function in oxidation and reduction simply by the opening and closing of the disulfide ring, but more recent study has shown that the matter is more complicated than that. There seems to be a  $\beta$ -lipoic acid, an oxidation product of the  $\alpha$ -lipoic.<sup>560</sup> A symposium on lipoic acid was held by the American Society of Biological Chemists in 1954.<sup>53.5, 136b, 289b, 295.5, 334.5, 370.5, 510.5, 557d, 611d, 650.5</sup>

Several have given accounts of the discovery, isolation, and synthesis of  $\alpha$ -lipoic acid.<sup>113.5, 126, 289a, 291, 527.5, 561</sup> Analysis showed it to contain two sulfur atoms to eight carbons and no nitrogen. Desulfurization gave caprylic acid. It was found possible to reduce it to a dimercaptan which could be oxidised back to the original acid. These facts pointed to a disulfide from a dimercaptocaproic acid.<sup>558, 559, 562</sup> It remained to find the location of the sulfur atoms. The 4,8-, 5,8-, and 6,8-dimercaptocaprylic acids were synthesized and oxidised to the disulfides. Of these only the 6,8-derivative showed the characteristic biological activity of the natural product.<sup>114, 127</sup> The structures of  $\alpha$ -lipoic acid and the dimercaptan are:<sup>335, 561</sup>

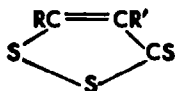


The addition of benzyl mercaptan to ethyl  $\zeta$ -octenoate gives an ester which is hydrolyzed to  $\epsilon$ -keto- $\eta$ -benzylmercaptocaprylic acid,  $\text{PhCH}_2\text{SCH}_2\text{CH}_2\text{CO}(\text{CH}_2)_4\text{CO}_2\text{H}$  (I). From this acid DL-lipoic acid has been synthesized in three ways. 1. This is reduced by sodium borohydride and the hydroxyl tosylated and treated with sodium benzylmercaptide. The resulting  $\epsilon, \eta$ -dibenzylmercaptocaprylic acid is debenzylated by sodium in liquid ammonia and the dimercapto-acid II oxidised. 2. The ketoacid, I, is converted to the dibenzyl mercaptole which is debenzylated to the dimercapto-acid II by sodium in liquid ammonia. 3. The ketoacid I is hydrogenated with sulfur, over a cobalt sulfide catalyst, to the dimercapto-acid II.<sup>632.5</sup>

$\epsilon, \eta$ -Dichlorocaprylic acid and benzyl mercaptan, in alkaline solution, give the dibenzylmercapto acid which is debenzylated.

$\epsilon,\eta$ -Dibromocaprylic acid is converted to the diacylmercapto acid by treatment with sodium thioacetate, this is hydrolyzed to the dimercaptoacid.<sup>561,5</sup>

### Trithiones



The trithiones constitute a newly recognized class of heterocyclics<sup>94, 263, 421</sup> which are produced by heating certain organic compounds with sulfur under particular conditions. The substituents R and R' may be alkyls or aryls. In trithione they are both hydrogen. Trithiones are also called 1,2-dithiole-3-thiones.

As sulfur may, and usually does, react with an organic compounds in several different ways simultaneously, a trithione is seldom, if ever, the sole product. The yields of trithiones are variable, frequently very low and in rare cases 90% or better. Organic compounds have been heated with sulfur since time immemorial and it is probable that chemists have had trithiones in their hands many times without recognizing them. Now that their characteristics are known it is much easier to isolate and identify them. In reviewing past chemical literature possible trithiones may be spotted here and there among the many compounds that have been described. Two clear cut examples are given, doubtless many such will come to light.

Back in 1880 Barbaglia heated *i*-valeraldehyde and sulfur to 250° in a sealed tube. By fractionation and recrystallization he isolated a bright yellow solid, melting at 94.5°. This had the composition  $\text{C}_5\text{H}_6\text{S}_3$  and was assigned the structure  $\text{H}_2\text{C}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHS}$ .<sup>49, 50</sup> Recently this experiment has been



repeated and the product shown to be the 4,5-dimethyltrithione.<sup>613</sup>

Erdmann in 1908 heated linalyl acetate with sulfur and got what he called a "thiozonide,"  $\text{C}_{12}\text{H}_{20}\text{O}_2\text{S}_3$ .<sup>213</sup> He imagined that the  $-\text{S}-\text{S}-\text{S}-$  added across a double bond like the three oxygen atoms in an ozonide. His product is now recognized as a trithione. The "thiozonides" from isophorone and from 2-methylindole do not appear to be trithiones.<sup>341, 548</sup> "Thiozonides" from

the sulfurizing of pinene<sup>582</sup> and terpenes<sup>376, 582</sup> were probably trithiones. Patents on gilding materials, later recognized as trithiones, claimed the addition of three atoms of sulfur to unsaturates.<sup>92</sup>

In a number of patented processes terpenes have been heated with sulfur under conditions which may have produced trithiones.<sup>100, 206, 260, 331, 365, 417, 464, 637c</sup> Sulfurizing dihydropentacene gives a product containing 41.65% sulfur which corresponds to the introduction of 6 atoms of sulfur.<sup>449</sup> When toluene vapor is passed through hot sulfur one molecule of it reacts with 5 atoms of sulfur, 3 of which remain and 2 pass off as hydrogen sulfide. These are the exact ratios for making a trithione. The product was a greenish brown solid but its sulfur content was too high.<sup>515</sup> Various other organic compounds give highly colored products with hot sulfur.<sup>417, 515, 516</sup> It was suggested by Erdmann that sulfur dyes might contain "thiozonides."<sup>213</sup> Trithiones should have been among the products from refluxing fenchyl alcohol with sulfur.<sup>691</sup> Indole and thianaphthene, heated with sulfur, give compounds of high sulfur content but those reported lack the characteristic color.<sup>657</sup> Lupeol and betulin have been sulfurized to what appear to be trithiones.<sup>80, 91</sup>

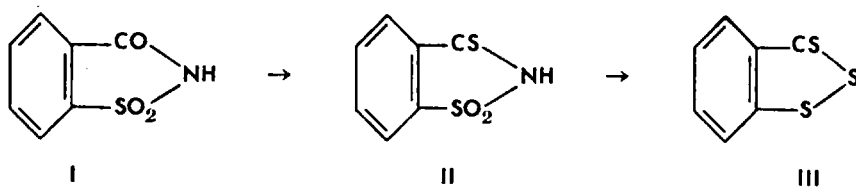
Sulfurizing dipentene, pulegone, carvone,<sup>589</sup> and  $\alpha$ -pinene<sup>540</sup> gives compounds containing four atoms of sulfur each. These may be trithiones with an extra sulfur somewhere in the molecule.

In the art of gilding chinaware it has long been the custom to heat turpentine, or some other hydrocarbon, with sulfur and to treat the sulfurized product with gold chloride. It is desirable to have a material of high metal content which blends well with oils to make the paint for decorating the ware. If everything is just right, when the ware is fired, the gold is left as a bright, continuous, adherent film. A possible reaction in the sulfurization of a terpene, at around 150°, is the formation of a mercaptan,  $C_{10}H_{15}SH$ , from which aurous mercaptide,  $C_{10}H_{15}SAu$  (Au 59.3%), might be derived. A product of approximately this composition has been used commercially. With more sulfur and at higher temperatures a trithione may be formed. A 65% yield of a trithione from pinene has been reported.<sup>94</sup> A trithione forms a complex with gold chloride and it is quite possible that trithiones have been present in some preparations of gilding mate-

rials. Complexes of gold salts with organic sulfides have been mentioned in chapter 2, volume II.

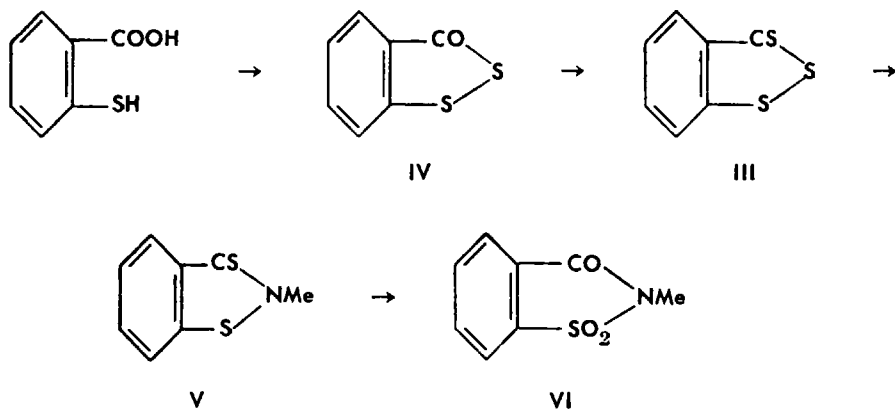
### Structure of Trithiones

The peculiar  $\text{—S—S—CS—}$  grouping was first recognized by Anna Mannessier in benzotrithione. Heating saccharin, I, with phosphorus pentasulfide at  $220^\circ$  gives thiosaccharin, II, in which the carbonyl oxygen has been replaced by sulfur. A second reaction, beginning at this temperature and becoming rapid at a slightly higher, produces the red benzotrithione, III.<sup>442</sup>



The red benzotrithione, III, was hydrolyzed by alkali to thiosalicylic acid.<sup>443</sup>

The structure of III was confirmed by a group of English chemists,<sup>435, 436, 437, 440, 627</sup> who worked in reverse, starting with thiosalicylic acid and ending up with N-methylsaccharin. Oxidation and condensation take place when thiosalicylic acid and hydrogen sulfide are dissolved in concentrated sulfuric acid with the formation of benzo-1,2-dithiole, or dithiobenzoyl, IV. The perthioacid,  $o\text{-HSSC}_6\text{H}_4\text{CO}_2\text{H}$ , has been suggested as an intermediate.<sup>627</sup> IV was converted to benzotrithione, III, by treatment with phosphorus pentasulfide. Methylamine replaced one of the sulfur atoms by  $>\text{NMe}$  giving V. This was oxidised by hydrogen peroxide to N-methylsaccharin VI.





What was later identified <sup>598</sup> as compound IV had been obtained in 1910 by heating the disulfide of thiosalicylic acid, but given another name and structure.<sup>325</sup>

Benzotrithione is obtained directly from thiosalicylic acid by treating it with phosphorus pentasulfide.<sup>236</sup> It has been prepared recently by sulfurizing 1-methylcyclohexene.<sup>407, 424</sup> Heating benzaldehyde with sulfur does not give it as might be expected.<sup>50</sup> *o*-Benzoic acid diselenide, (*o*-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>Se)<sub>2</sub>, with this reagent, gives the compound with selenium in the 1-position, while with phosphorus pentaselenide the triselenone is formed.<sup>4</sup>

The significance of these results on benzotrithiones does not seem to have been fully appreciated by later investigators on trithiones.

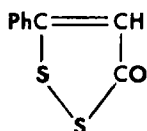
Our knowledge of the chemistry of the trithiones is a composite of the findings of several groups of chemists, working independently in several countries and more or less simultaneously. As much of the work was done during World War II, when the publication of articles and the issuing of patents were delayed, there was some duplication of effort. While there were differences in their approaches and in the details of their experiments all of the investigators came to essentially the same conclusions. Trithiones have been reviewed.<sup>55</sup>

The first trithione identified as such was the one from anethole and this is the one that has been used most extensively in working out the chemistry of the group.<sup>94</sup> Years ago anise oil was heated with sulfur to make "anisated balsam of sulfur,"<sup>444</sup> which may, or may not, have contained some of the trithione. The proportion of sulfur was low and the temperature was probably not high enough to produce any appreciable amount. The use of anethole in ceramic materials led to the discovery of the trithiones.<sup>94</sup> To prepare the trithione, anethole is heated with 87% of its weight of sulfur. At 175° the evolution of hydrogen sulfide begins and a spontaneous reaction sets in which takes the temperature up to 240°. The mixture is stirred for an hour at 220°. As the reported yield is around 53%, it is evident that other reactions take place.<sup>94</sup>

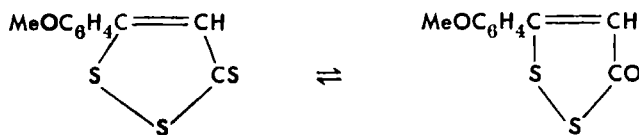
The product is a bright orange-red solid. It contains no labile hydrogen, hence is not an acid or a mercaptan. It forms addition compounds with gold and mercury chlorides.<sup>94</sup> Oxidation converts it to anisic acid <sup>94, 262</sup> and so does heating it with potassium

hydroxide in the absence of air. These facts show that the methoxyl group and the benzene ring are not involved in the formation of the trithione and that all of the sulfur is attached to the 3 carbon chain. The formation of an oxime shows the presence of the  $>CS$  group. Two atoms of sulfur are removed as sodium sulfide by sodium and ethanol. Only the terminal carbon of the  $-CH:CHCH_3$  side chain could be sulfurized to  $>CS$ . A consideration of these facts led to the trithione structure with the *p*-methoxyphenyl in the 5-position.<sup>94</sup> The fact that this trithione takes up two atoms of chlorine, bromine or iodine<sup>423</sup> has been taken to show that the double bond of anethole is still present. The reaction of trithiones with halogens will be taken up later. Adducts are formed with alkyl halides, the decomposition of which gives mercaptans, showing that the attachment is to the  $>CS$  group.<sup>427</sup>

Back in 1897 Baumann and Fromm heated ethyl cinnamate with sulfur and got a dithione,  $C_9H_6OS_2$ , to which they assigned the structure:



Treating this with phenylhydrazine gave 1,3-diphenylpyrazolone-5.<sup>60</sup> This work has been repeated and *p*-methoxycinnamic ester given the same treatment. Both of the products were treated with phosphorus pentasulfide, the accepted method for converting a carbonyl group to the thione,  $>CS$ .<sup>93a</sup> The one from *p*-methoxycinnamic ester proved to be identical with the trithione from anethole. Conversely the  $>CS$  group can be oxidised to the carbonyl,<sup>261</sup> thus the trithione from anisole, treated with mercuric acetate<sup>91</sup> or permanganate<sup>262, 421, 684</sup> is converted to the dithione obtained by the sulfurization of *p*-methoxycinnamic ester:<sup>91</sup>



The same reciprocal transformations have been demonstrated for the corresponding 5-phenyl compounds.<sup>430, 684</sup> The sulfurization

of a dithione to a trithione is a perfectly general reaction as is the oxidation of a trithione to a dithione.

5-(*p*-Hydroxyphenyl)-trithione is obtained by demethylating the *p*-methoxy compound by pyridine hydrochloride.<sup>589</sup>

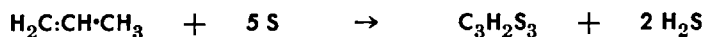
When a cinnamic ester having a methyl group in the side chain is sulfurized the methyl group is attacked and the product is a carboxytrithione instead of a dithione.<sup>83a, 425, 589</sup>

Sulfurizing unsaturated esters gives dithiones which can be changed to trithiones by treatment with phosphorus pentasulfide. It has been found possible to combine these two treatments. The ester is heated with a mixture of sulfur and phosphorus pentasulfide. Cinnamic ester reacts satisfactorily at 130°. <sup>430</sup> 4,5-Dimethyltrithione has been made in this way from angelic and tiglic esters and from the acetoacetic ester, MeCOCHMeCO<sub>2</sub>Et, which in its enol form is an unsaturated ester.<sup>162, 428</sup> Cinnamic alcohol and aldehyde give the trithione with sulfur alone.<sup>684</sup>

Trithiones are prepared from β-keto-esters and phosphorus pentasulfide in boiling xylene. 2-Carbethoxycyclopentanone and 2-carbethoxycyclohexanone give bicyclic trithiones.<sup>424</sup> Propiophenone and its *p*-methoxy- derivative heated with sulfur and phosphorus pentasulfide, give trithiones with the phenyl group in the 5-position.<sup>422</sup>

### Formation of Trithiones

As the trithione ring contains the grouping, —CH:CH·CS·S—, the starting material must have a chain of three carbon atoms two of which should be joined by a double bond and the third should be a primary carbon. Propylene is the simplest hydrocarbon that meets these conditions. When it is passed over sulfur at 220–50° trithione is formed but the yield is poor.<sup>430</sup> The reaction conditions are not favorable. The solubility of the gas in sulfur at that temperature must be very low. Pressure might be used to improve the contact but two molecules of hydrogen sulfide are given off for one of propylene that reacts:

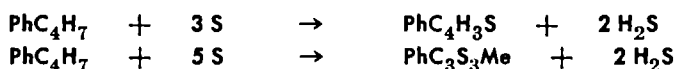


In anethole, *p*-MeOC<sub>6</sub>H<sub>4</sub>CH:CHCH<sub>3</sub>, the side chain is just right for trithione formation and its boiling point, 235°, is sufficiently high for it to remain in the reaction mixture while the hydrogen sulfide escapes. Its isomer estragole, MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-

CH:CH<sub>2</sub>, gives the same trithione under the same conditions<sup>262, 589</sup> but the yield is lower.

Eugenol, 4,3-HO (MeO)C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CH:CH<sub>2</sub>, and isoeugenol, 4,3-HO (MeO)C<sub>6</sub>H<sub>3</sub>CH:CHMe, give the same trithione.<sup>94, 421</sup> Only one is possible. Isomerization may take place, either before or during the sulfurization. The same holds for the formation of trithiones from similar pairs, safrole and isosafrole,<sup>94</sup> allylbenzene and propenylbenzene.<sup>683, 684</sup> The phenyl group will be found in the 5-position in the resulting trithione. Aromatics having allylic or propenyl side chains are particularly suitable for the preparation of trithiones.<sup>91, 93a, 683, 684</sup> The sulfuration of anethole may be effected even in boiling toluene in the presence of a tertiary amine.<sup>389</sup>  $\alpha$ -Methylstilbene goes to 4,5-diphenyltrithione.<sup>684</sup>

When there are just three carbons in the aliphatic side chain the attack by the sulfur is confined to them and the product is apt to be a trithione. When there are four or more carbons a thiophene may be formed.<sup>686</sup> Thus 1-phenylbutene-1 and 4-phenylbutene-1 give 2-phenylthiophene<sup>685</sup> and 2-phenyl-3-methylbutadiene goes to 3-methyl-4-phenylthiophene.<sup>683</sup> It could not generate a trithione without breaking a carbon to carbon bond. 2-Phenylbutene-2 gave 3-phenylthiophene.<sup>116</sup> The formation of 4-phenyl-5-methyltrithione from this hydrocarbon looks possible. It is interesting to write the stoichiometric equations for the formation of the two:



Other things being equal a higher sulfur ratio should favor trithione formation. Two molecules of hydrogen sulfide are evolved in each case and the phenylthiophene and methylphenyltrithione contain the same number of hydrogen atoms. In many cases it is likely that both are formed, the relative amounts depending on reaction conditions as well as on the structure of the starting materials. In the case of 2-(*p*-methoxyphenyl)-butene-2, a good yield of 4-*p*-methoxyphenyl-5-methyltrithione was isolated along with some of the 3-*p*-methoxy-phenylthiophene.  $\alpha$ -Methylstyrene gives a good yield of the trithione,<sup>589, 684</sup> though it does not react as rapidly as its *p*-methyl and *p*-methoxy derivatives.<sup>589</sup>

Unsaturation in the side chain of starting materials is not necessary. It may well be that the sulfur splits off hydrogen and

then reacts with the resulting unsaturate. Cumene gives a high yield of the 4-phenyl-trithione. An alkyl group in the para position influences the reaction velocity. *p*-Cymene reacts 4.9 times as fast, *p*-ethylcumene 1.8 times and *p*-*t*-butyl only half as fast.<sup>230</sup>

Methylphenylacetylene,  $\text{PhC}:\text{CMe}$ , and propiophenone are sulfurized to 4-phenyltrithione.<sup>422</sup> Quite unexpected was the finding of some trithione and its isomer, vinylene trithiocarbonate, along with thiophene and other products when acetylene and sulfur were heated to  $450^\circ$ . These may have been formed by the addition of sulfur and carbon disulfide to acetylene or from acetone in the acetylene.<sup>151</sup>

Trithione formation is aided greatly by the presence of catalytic amounts of tertiary amines.<sup>230, 389</sup> In a recorded experiment a toluene solution of anethole and sulfur was refluxed. In 10 hours 90% of the sulfur had reacted.<sup>389</sup>

Isobutylene gives 4-methyltrithione.<sup>634</sup> When the double bond is farther from the end of the chain than the  $\beta$ -position the necessary methyl group must be a branch. Thus *i*-amylene, 2-methylbutene-2, gives 4,5-dimethyltrithione.<sup>117, 613, 634</sup> This is the same trithione that is formed when *i*-valeraldehyde is heated with sulfur. It is to be remembered that *i*-amyl alcohol and the aldehyde from it, are mixtures. Of the two isomers, only II should form this trithione:



### Mechanism of Trithione Formation

Nothing even approaching a complete picture can be given, but facts are known from which some inferences can be drawn. When a hydrocarbon is heated with sulfur various reactions may take place, simultaneously and consecutively. Which of these predominate and what the final products will be depend on the nature of the hydrocarbon and the reaction conditions, particularly the temperature and the proportion of sulfur. At higher temperatures hydrogen sulfide and other volatile products may escape from the reaction zone unless kept in by pressure. Trithione formation has been considered to be conditioned by the

presence of unsaturates of a particular structure. As dehydrogenation and shifting of double bonds may take place during the heating, trithiones are sometimes obtained from materials in which the double bond is not properly placed or is even absent.<sup>244</sup> Particularly at higher temperatures, thiophenes may be formed.

It is now generally accepted that the attack by sulfur is on the hydrogen of the methylene group,  $-\text{CH}_2-$ , adjacent to the double bond.<sup>684</sup> The importance of the double bond seems to be in that it facilitates and directs this attack to the proper place. With a saturated hydrocarbon the location of the point of attack is a matter of chance and further sulfurization may not lead to a trithione. Thus isooctane gives some of a trithione<sup>244</sup> but much less than does diisobutylene.

The results of an investigation intended to throw light on the vulcanization of rubber<sup>223</sup> are of interest in this connection. Each of three unsaturated hydrocarbons, cyclohexene, 1-methylcyclohexene and isobutene, was heated with sulfur for 5 hours at  $140^\circ$ . The molecular ratio of hydrocarbon to sulfur was around 1:1 instead of 1:5 required for trithione formation. Negligible amounts of thiols and of hydrogen sulfide were found in the products. This does not prove that these had not been formed. Hydrogen sulfide may have combined with the unsaturate to give a mercaptan. Mercaptans combine with unsaturates to form sulfides<sup>356</sup> and are converted to disulfides and polysulfides by sulfur.<sup>430</sup> The fact that only small amounts of monosulfides were found in the products from the first two and none in that from the third may be taken to indicate that hydrogen sulfide and mercaptans have not been important factors. Alkyl sulfides, once formed, are not converted to disulfides under these conditions. The products isolated from the cyclohexene experiment had the composition,  $\text{C}_6\text{H}_9\text{S}_x\text{C}_6\text{H}_{11}$  in which  $x$  is from 1 to 6 but chiefly 2, 3, 4 and 5. With isobutylene  $x$  was 2, 3 and 4. It is possible, but hardly probable, that  $\text{C}_6\text{H}_9\text{S}_x\text{C}_6\text{H}_{11}$  may have been a mixture of equal amounts of  $\text{C}_6\text{H}_9\text{S}_x\text{C}_6\text{H}_9$  and  $\text{C}_6\text{H}_{11}\text{S}_x\text{C}_6\text{H}_{11}$ . An explanation, which may not be correct, but which fits the known facts, is that the  $\text{S}_8$  molecule breaks into fragments  $-\text{S}-$ ,  $-\text{S}\cdot\text{S}-$ ,  $-\text{S}\cdot\text{S}\cdot\text{S}-$ , etc. and that one of these attacks the  $-\text{CH}_2-$  adjacent to the double bond:



The addition of these to cyclohexene may follow:

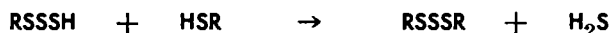


The polysulfides being capable of giving off, or taking up sulfur, are in equilibrium with each other and with sulfur.<sup>223</sup>

In another investigation<sup>117</sup> three unsaturated hydrocarbons, 2-methylbutene-2, pentene-2 and 2,3-dimethylbutene, were sulfurized at 170°. The products from 2-methylbutene-2 were: a thiol,  $\text{Me}_2\text{C}:\text{CHCH}_2\text{SH}$ , which may have been partly the isomeric  $\text{MeCH}:\text{CMeCH}_2\text{SH}$ , a sulfide,  $\text{C}_{10}\text{H}_{20}\text{S}$ , a disulfide,  $\text{C}_{10}\text{H}_{20}\text{S}_2$ , a trisulfide,  $\text{C}_{10}\text{H}_{20}\text{S}_3$ , 4,5-dimethyltrithione and a non-volatile residue, from which some pentasulfide was isolated. The amounts of thiol and monosulfide were negligible. Oxidation of the disulfide gave acetone, which indicates that one of the alkyls had the structure assigned to the alkyl of the thiol. The results were explained, as above, by assuming that a fragment of the  $\text{S}_8$  molecule displaces a methylene hydrogen to form a mercaptan,  $\text{C}_4\text{H}_7\text{S}_x\text{H}$ , which attaches itself to the isoamylene to form the polysulfide,  $t\text{-AmS}_x\text{C}_4\text{H}_7$ ,  $\text{C}_{10}\text{H}_{20}\text{S}_x$ . The products isolated from the sulfurization of pentene-2 were the disulfide,  $\text{C}_{10}\text{H}_{20}\text{S}_2$ , the trisulfide,  $\text{C}_{10}\text{H}_{20}\text{S}_3$  and 5-ethyltrithione. With 2,3-dimethylbutene-2 the principal product was the trisulfide,  $\text{C}_{12}\text{H}_{24}\text{S}_3$ . No trithione was found.

In an earlier study of the sulfurization of 2-methylbutene-2 at 120 to 140°, sulfides and disulfides containing the groups,  $-\text{SCH}_2\text{CMe}:\text{CHMe}$ ,  $-\text{SCHMeCMe}:\text{CH}_2$ , and  $-\text{SCH}_2\text{CH}:\text{CMe}_2$ , were isolated.<sup>12</sup> This shows that the sulfur had attacked the hydrocarbon at all possible places. The principal attack was on the 1-carbon. If the hydrocarbon is written  $(\text{H}_3\text{C})_2\text{C}:\text{CHCH}_3$  it can be seen that there are six chances for this to three for the 4-carbon and one for the 3-carbon.

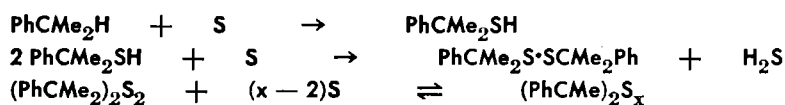
Attention is called to two other ways in which polysulfides may be formed. A perthiomercaptan might react with a mercaptan:



Or a mercaptan might be sulfurized to a disulfide which would take up additional sulfur. In either of these hydrogen sulfide would be formed. The addition of this to the amylene would give *t*-amyl mercaptan, the sulfurization of which would give

*t*-amyl polysulfide,  $C_{10}H_{22}S_x$ . This contains more hydrogen than the polysulfide,  $C_{10}H_{20}S_x$  accounted for by the above theory. In an investigation of the sulfurization of 2-methylbutene-2 attention was called to the fact that the polysulfides had more hydrogen than that calculated for  $C_{10}H_{20}S_x$ .<sup>613</sup> In the sulfurization of dipentene,  $C_{10}H_{16}$ , a trisulfide,  $C_{10}H_{18}S_3$ , was obtained.<sup>93a</sup> This may have been formed by the addition of two molecules of hydrogen sulfide and the sulfurization of the product.

Recent experiments on the sulfurization of cumene and *p*-cymene lead to improved methods for preparing certain trithiones and also throw light on the reactions involved.<sup>230</sup> In one run 1108 g. of *p*-cymene was refluxed 20 hours with 400 g. of sulfur and 8.2 g. of di-*o*-tolylguanidine. On cooling, 355 g. of 4-*p*-tolyltrithione crystallized out. Topping off the excess *p*-cymene left 330 g. of a heavy liquid which was shown, by analysis and other tests, to be the disulfide,  $MeC_6H_4CMe_2SSCMe_2C_6H_4Me$ . It was colored red and contained 19.70% sulfur instead of the calculated 19.39%, indicating a trace of the trithione. Adding the amount of sulfur in these two products to that which must have been in the hydrogen sulfide evolved in their formation accounts for the sulfur used. The results may be accounted for by assuming that the *p*-cymene was sulfurized to the mercaptan, that the mercaptan was converted to the disulfide and that the disulfide took up sulfur which was used up in sulfurizing a part of the polysulfide to trithione:

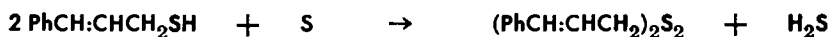


It is well known that amines facilitate the conversion of mercaptans into disulfides by sulfur and also the passage of disulfides into polysulfides and the reverse reaction. It has been shown that alkyl polysulfides are prime sulfurizing agents.<sup>356</sup> In this case the polysulfides, which must have been intermediates, were reduced so completely to the disulfide that the sensitive copper strip test was negative.

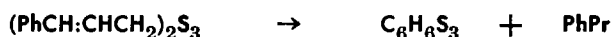
The ease with which *p*-cymene is sulfurized to the trithione is due to the extreme lability of the tertiary hydrogen. Cumene gave equally as good results though it did not react so rapidly. Under the same conditions the isomeric *n*-propylbenzene did not react.<sup>230</sup>



It has been shown that cinnamyl mercaptan gives 5-phenyltrithione when it is heated with sulfur. The mercaptan and sulfur react readily:



Even at 50° this reaction is 62% complete in 2 hours. This disulfide and sulfur give the trithione. The trisulfide, when heated without additional sulfur, gives the trithione and propylbenzene:

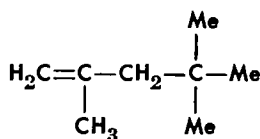


The hydrogen that is displaced from one cinnamyl radical saturates the other.<sup>430</sup> The reaction is certainly not as simple as it is written.

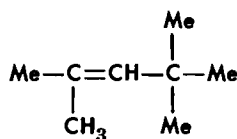
These experiments show that trithione formation proceeds readily once the methyl contains sulfur. They have nothing to say about the point of attack of sulfur on an unsulfurized hydrocarbon. It has been suggested that the mercaptan is sulfurized to the thioaldehyde,  $\text{PhCH:CHCHS}$  and then to dithiocinnamic acid,  $\text{PhCH:CHCSSH}$ .<sup>684</sup> This would not fit the case of a tertiary mercaptan such as  $\text{PhCMe}_2\text{SH}$ .

Trithiones have been made from *i*-amyl sulfide and disulfide and from *i*-butyl disulfide. The branching of the chain makes quite a difference:  $n\text{-Bu}_2\text{S}_2$  gave 3% and *i*- $\text{Bu}_2\text{S}_2$  13% and  $n\text{-Am}_2\text{S}_2$  3% and *i*- $\text{Am}_2\text{S}_2$  16%.<sup>695</sup>

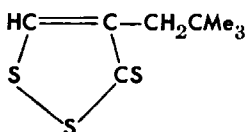
The formation of trithiones from the two diisobutylenes is of particular interest and has been studied with care.<sup>634, 644, 645</sup> The structures of the diisobutylenes, A and B, are such that there are only two positions in which a double bond can be located and there are only two possible trithiones, I and II.



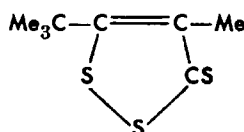
A



B



I 4-Neopentyltrithione

II 4-Methyl-5-*t*-butyltrithione

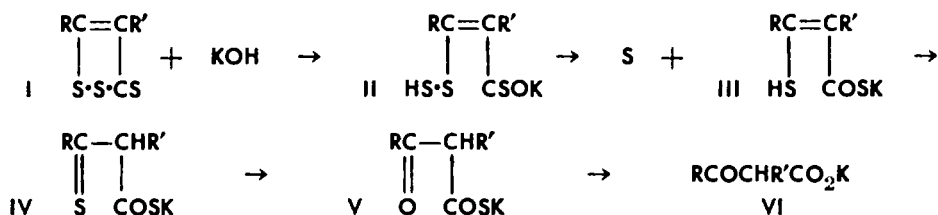
From these structures it would be expected that the isomer A would give the trithione I and that II would come from B. Curiously enough, each of the isomers, A and B, gives both of the trithiones, and in approximately the same ratio, two of I to one of II. In both the carbon of the 2-methyl group is the one that is completely sulfurized, whether or not it is the one first attacked. The presence of a double bond is important but it may shift its position.

As two molecules of hydrogen sulfide are formed to one of the trithione its pressure builds up rapidly when the reaction is carried out in a closed system. The yield of trithione is much larger when the hydrogen sulfide is vented so that its pressure does not exceed 60 pounds.<sup>644</sup>

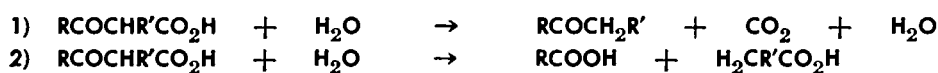
### Reactions of Trithiones

#### Alkaline Hydrolysis

Observed facts show quite well what reactions take place but their exact sequence is not clear. Two atoms of sulfur are removed as sodium sulfide<sup>94</sup> and the third as sulfur. The reactions have been formulated as follows:<sup>428</sup>



The product is an  $\alpha$ -alkyl-, or  $\alpha$ -aryl-, acetoacetic acid which may hydrolyze in either of two ways:



Methyl ethyl ketone was obtained from 4,5-dimethyltrithione.<sup>428</sup> The presence of  $p\text{-MeOC}_6\text{H}_4\text{COCH}_2\text{CO}_2\text{H}$  as an intermediate in the hydrolysis of the anethole trithione was proved by the isolation of the ketone,  $p\text{-MeOC}_6\text{H}_4\text{COMe}$ .<sup>589</sup> The anisic acid which is produced<sup>94</sup> can come from the same intermediate. The hydrolysis of 4-methyl-5-phenyltrithione gave benzoic acid.<sup>684</sup>

The hydrolysis of the unsubstituted trithione, in which R and R' are H, gave formic and acetic acids according to reaction 2.<sup>151</sup>

The hydrolysis of 4-methyltrithione, in which R' is methyl gave formic and propionic acids. The hydrolysis of 4-neopentyltrithione, in which R=H and R'=Me<sub>3</sub>C·CH<sub>2</sub>, gave formic acid and γ,γ-dimethylvaleric acid, Me<sub>3</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, mixed with some of the corresponding thioacid, Me<sub>3</sub>CCH<sub>2</sub>CH<sub>2</sub>COSH, indicating that splitting went on before the last sulfur atom was eliminated. Similarly from 4-methyl-5-*t*-butyltrithione, in which R'=Me and R=Me<sub>3</sub>C, propionic and pivalic, Me<sub>3</sub>C·CO<sub>2</sub>H, acids were obtained. Besides these some ethyl *t*-butyl ketone was isolated, which had been formed according to reaction 1.<sup>634</sup> This has been claimed as a method of preparing γ,γ-dimethylvaleric acid.<sup>633</sup>

In these three hydrolysis experiments the production of dimethyl sulfide and disulfide by treatment of the alkaline solution with dimethyl sulfate showed the presence of sodium sulfide and disulfide. The liberated sulfur had combined with a part of the sodium sulfide.

The formation of trithiones from β-keto-esters has been noted above. The hydrolysis of trithiones to β-keto-acids, here postulated, is essentially a reversal of this. Sodium hydroxide acts also as a desulfurizing agent.

The hydrolysis of 5-phenyldithione appears to follow the same course as that of the trithione. The presence of PhC(SH):-CHCOSH, III in the above scheme, was shown by the formation of PhC(SCH<sub>2</sub>CO<sub>2</sub>H):CHCOSH<sub>2</sub>CO<sub>2</sub>H when sodium chloroacetate was added.<sup>243</sup> Ammonia replaces the sulfur atom in the 2-position by > NH to form 2-thiobenzimide.<sup>440</sup> An amine gives the N-alkylimide. The imide can be reduced and then oxidised to the amide of the disulfide of thiosalicylic acid, (o-H<sub>2</sub>NCOC<sub>6</sub>-H<sub>5</sub>S·)<sub>2</sub>.<sup>434, 435</sup>

### Other Reactions

Grote's reagent gives purple-red<sup>117</sup> or cherry-red<sup>684</sup> colors with trithiones. They are oxidised by hydrogen peroxide, or nitric acid, to sulfuric acid. 4-Methyl-5-phenyltrithione gives benzoic acid also.<sup>684</sup>

Trithiones take up chlorine,<sup>423, 684</sup> bromine, and iodine.<sup>117, 423, 684</sup> Chlorine replaces the thione sulfur by chlorine, converting > CS to > CCl<sub>2</sub>.<sup>476, 634</sup> Thionyl and sulfonyl chlorides couple two molecules of a trithione together.<sup>476</sup> Iodine is said to convert a trithione to a disulfide, involving the thione sulfur.<sup>423, 427</sup>

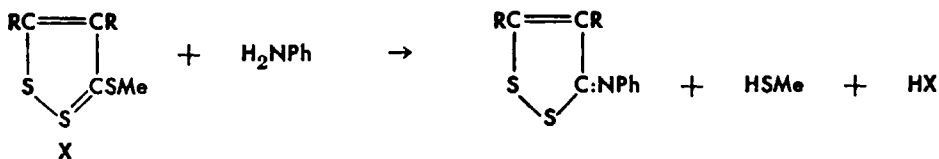
Trithiones form adducts with mercuric chloride<sup>93a, 94, 151, 162, 421, 423, 424, 634, 684</sup> and bromide,<sup>117, 684</sup> silver nitrate,<sup>94, 151, 684</sup> cuprous bromide,<sup>684</sup> cupric chloride,<sup>151</sup> and with the chlorides of antimony,<sup>423, 476</sup> tin,<sup>421, 423, 476</sup> zinc, cadmium,<sup>684</sup> gold,<sup>94, 684</sup> bismuth,<sup>476, 684</sup> platinum, palladium, and iron.<sup>684</sup> The 4-phenyl-, 5-phenyl-, and 4-methyl-5-phenyl-trithiones have been recommended as reagents for the detection of silver, gold, mercury, tin, platinum, and palladium.<sup>687</sup>

Trithiones are soluble in concentrated acids and are precipitated unchanged on dilution.<sup>162, 684</sup>

### Trithionium Salts

Trithiones combine with alkyl halides or sulfates.<sup>55, 93a, 94, 117, 151, 230, 421, 427, 428, 634, 684</sup> This subject has been summarized.<sup>431</sup> The reaction is similar to the addition of halides to thiourea. The alkyl attaches itself to the carbonyl sulfur and the product is a salt. From analogy to the isothiuronium salts these have been called trithionium salts. The adjacent sulfur atom takes on sulfonium characteristics. The orange color of a trithione becomes lighter when it passes into a trithionium salt.<sup>431</sup> The trithionium salt from 3,4-dihydroxyphenyltrithione changes from orange to blue when its solution is made alkaline, indicating a shift to a quinoid form.<sup>431</sup> When heated, an alkyltrithionium salt dissociates into its original components. Methyltrithionium iodide has been shown to be a methylating agent. Whether this is due to the trithionium salt or to the methyl from its decomposition has not been demonstrated.

The most interesting reaction of the trithionium salts is that with amines. This is analogous to the reaction of isothiuronium salts with amines but proceeds more readily. With aniline the mercaptan is displaced and an anil is formed:



*p*-Aminobenzoic acid and *p*-dimethylaminoaniline react similarly. Hydrazine gives an azine while hydrazones give mixed azines. Hydrazine can be used to couple a trithionium salt with a carbonyl compound, such as pyruvic acid. Trithiones do undergo

reactions of this type but much more slowly and with poorer yields.

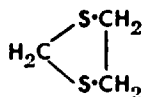
### Physiological

The only trithione that has been investigated extensively is the one from anethole. It stimulates the liver,<sup>296, 386, 387</sup> increases bile secretion,<sup>296, 386, 387</sup> and causes an increase in nitrogen metabolism.<sup>387, 431</sup> Taken by mouth it shows low toxicity.<sup>55</sup> Their water-soluble sulfonium salts have some disinfectant activity.<sup>55</sup> The activity remains when the thione sulfur is replaced by nitrogen as in the oxime. It is even greater in the mixed azine.<sup>431</sup>

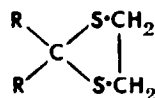
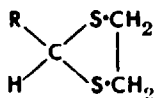
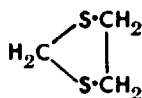
### Applications

So far the possible applications of trithiones have not been explored sufficiently to show the extent of their usefulness. The mixture of the two from diisobutylene is claimed as a fuel additive.<sup>645, 646</sup> Trithiones have a marked affinity for metal surfaces and are excellent protective agents particularly for iron. This is attributed to the identity of the S—S distance in the trithione and the Fe—Fe distance in  $\alpha$ -iron.<sup>427</sup> Trithiones have been compared with other pickling inhibitors in hydrochloric, sulfuric, and acetic acids. They rate high in effectiveness.<sup>429</sup> They have been recommended as additions to high pressure lubricants<sup>617</sup> and to cutting oils.<sup>644</sup> The 4-aryl-, 5-aryl-, 4,5-diaryl-, and 4-methoxyaryltrithiones have been claimed as constituents for lubricating oils.<sup>4</sup> They have been the subjects of numerous patents.<sup>55, 92, 206, 260, 261, 376, 645, 646</sup>

### Dithiolane



The best known derivatives are mercaptals and mercaptoles which are obtained from ethylene mercaptan with aldehydes or ketones.



Usually the preparation of these is a simple matter; the calculated amounts of the reactants are mixed and hydrogen chloride is passed in. With aldehydes the reaction is usually rapid, the mixture becoming cloudy with the first bubbles of hydrogen chloride. Ketones react more slowly. The reaction may be started with concentrated hydrochloric acid, instead of the gaseous hydrogen chloride. When it appears to have gone as far as it will, the separation of the water layer may be aided by the addition of some syrupy zinc chloride.<sup>564</sup> The water layer is separated and the remaining mixture resaturated with hydrogen chloride. Zinc chloride may be added to push the reaction to completion, but this is seldom necessary. The yields are usually practically quantitative. Recently boron trifluoride etherate has been recommended as a catalyst. This has given excellent results in the few cases in which it has been used.<sup>231</sup>

Dithiolanes have been prepared from formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, and anisaldehyde and from acetone, benzophenone, pyruvic acid, and a number of other ketones, including some cyclic.<sup>316, 317, 318, 564</sup> The majority of those that are known are viscous liquids or low melting solids. They are more stable to heat than mercaptals or mercaptoles of comparable molecular weight from univalent mercaptans. Thus  $\text{MeCH}(\text{SCH}_2\cdot)_2$  can be distilled at atmospheric pressure, while acetone diethylmercaptol,  $\text{Me}_2\text{C}(\text{SEt})_2$ , can not be. Some of these dithiolanes have been oxidised to the disulfones, but this does not always go smoothly.<sup>225</sup>

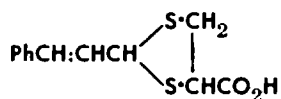
1,3-Dithiolane,  $\text{CH}_2(\text{SCH}_2\cdot)_2$ , the simplest member of this group, is less easy to prepare than the higher members.<sup>62</sup> The best method is to distill a mixture of formaldehyde and sodium ethylene thiosulfate.<sup>270</sup> It has been prepared by the reaction of ethanedithiol with formaldehyde<sup>151</sup> or with methylene chloride.<sup>671</sup> The mercuric chloride addition product and a methiodide are known.<sup>270</sup>

A double compound,  $(\cdot\text{CH}_2\text{S})_2\text{CH}\cdot\text{CH}(\text{SCH}_2\cdot)_2$ , has been made from glyoxal.<sup>225, 545</sup> From ethylene mercaptan and ethyl orthoformate a compound has been prepared which may have the formula,  $(\cdot\text{CH}_2\text{S})_2\text{CHSCH}_2\text{CH}_2\text{SCH}(\text{SCH}_2\cdot)_2$ , and belong to this class. Hexanedithiol-1,2 condenses with acetone to 2,2-dimethyl-4-butyl-1,3-dithiolane.<sup>36</sup>

2,3-Dimercaptopropanol condenses with aldehydes and ketones to give dithiolanes substituted in the 2-position and having  $-\text{CH}_2\text{OH}$  in the 4-position.<sup>532, 649</sup>

Ethylene mercaptan reacts with only one of the ketone groups in benzil to give 2-phenyl-2-benzoyl-1,3-dithiolane. *o*-Dimercaptobenzene reacts similarly with benzil and with diacetyl.<sup>343</sup> Ethane-1,2-di-*p*-toluenesulfonate and desoxybenzoin are condensed by potassium acetate in alcohol to 2-phenyl-2-benzoyl-1,3-dithiolane.<sup>158</sup> Phenacylidene dimercaptan and ethylene bromide react in alkaline solution to give 2-phenacylidenedithiolane,  $\text{PhCOCH}:\text{CH}(\text{SCH}_2)_2$ . The thiophene analog,  $\text{C}_4\text{H}_3\text{S}\cdot\text{COCH}:\text{CH}(\text{SCH}_2)_2$ , has been prepared similarly.<sup>366a</sup> Dithiolanes have been prepared from cholestanone and other steroid ketones with the aid of boron trifluoride etherate.<sup>231</sup>

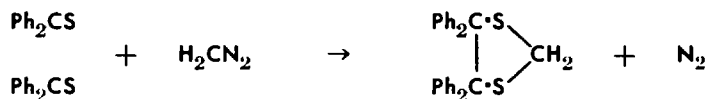
The ester,  $(\cdot\text{CH}_2\text{S})_2\text{CHCOOEt}$ ,<sup>150, 367</sup> and the corresponding acid,  $(\cdot\text{CH}_2\text{S})_2\text{CHCOOH}$ , are known.<sup>150, 158, 367</sup> Cinnamaldehyde and  $\alpha,\beta$ -dimercaptopropionic acid give an acid:<sup>571</sup>



Similarly 1,3-dithiolanes are obtained from acetone and 2,3-dimercaptopropionic acid or its esters.<sup>398, 530</sup>

Ethylene trithiocarbonate,  $(\cdot\text{CH}_2\text{S})_2\text{CS}$ , has the ring structure which puts it in this group, but it seems best to consider it along with other trithiocarbonic esters in Volume 4.

By the action of diazomethane on thiobenzophenone 4,4,5,5-tetraphenyl-1,3-dithiolane is formed:

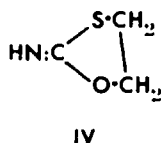
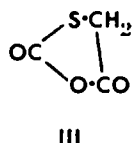
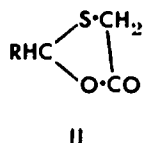
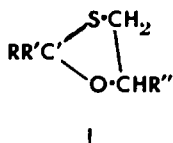


Diazoethane and diazoacetic ester give the 2-methyl- and 2-carbethoxy derivatives.<sup>596</sup> 4-Thiochromone,<sup>597, 599</sup> thioxanthione, and other aromatic thioketones<sup>597</sup> react similarly.

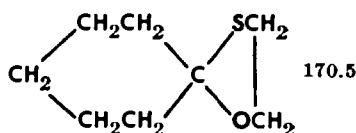
The condensation of ethyl 1-carbethoxy-2-oxocyclohexanecarboxylate with ethanedithiol gives 6-(3-carbethoxypropyl)-6-carbethoxy-1,4-dithiaspiro-[4,5]-decane, one ring of which has this structure.<sup>667</sup>

Compounds of this ring structure but having one sulfur atom replaced by oxygen have been obtained in several ways: from

an aldehyde, or ketone, with mercaptoethanol or one of its derivatives (I),<sup>197, 373, 624b</sup> from the lactonization of a hydroxysulfide acid,  $\text{RCH}(\text{OH})\text{SCH}_2\text{CO}_2\text{H}$ , (II),<sup>329, 395a, 395b, 395d</sup> from thioglycolic acid and phosgene (III),<sup>180, 181</sup> or from  $\beta$ -hydroxyethyl thiocyanate (IV).<sup>615, 616</sup>

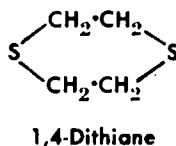
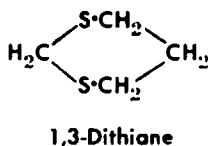
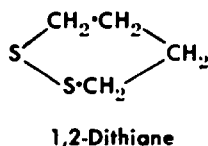


Cyclohexanone and mercaptoethanol give the spiro compound,



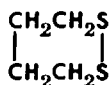
## TWO SULFUR AND FOUR CARBON ATOMS

The sulfur atoms can be in the 1,2-, 1,3-, or 1,4-positions giving the unsubstituted rings:



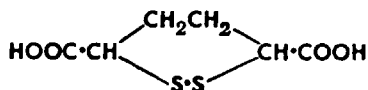
Of these the 1,4- and its derivatives are the best known and the 1,2- the least.

### 1,2-Dithiane



1,2-Dithiane has been made by treating 1,4-tetramethylene dithiocyanate with potassium hydroxide<sup>111.5</sup> and also by the reaction of tetramethylene bromide and sodium disulfide.<sup>53.7</sup> Its preparation from the Bunte salt has been mentioned earlier.<sup>2</sup>

The oxidation of  $\alpha,\alpha'$ -dimercaptoadipic acid gives a 1,2-dithiane derivative:<sup>238d</sup>

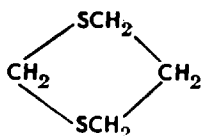




The meso melts at  $199^\circ$  and the racemic at  $275^\circ$  with decomposition. The latter has been separated into the active forms which melt at  $257^\circ$  and have the rotations  $[\alpha]_{25/D} +336.6^\circ$  and  $-335.8^\circ$ .<sup>238d</sup> The selenium analog has been reported.<sup>239a, 239b, 239c</sup>

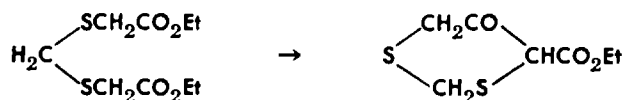
The 3,6-dimethyl derivative has been prepared from acetylacetone and hydrogen sulfide.<sup>133</sup>

### 1,3-Dithiane



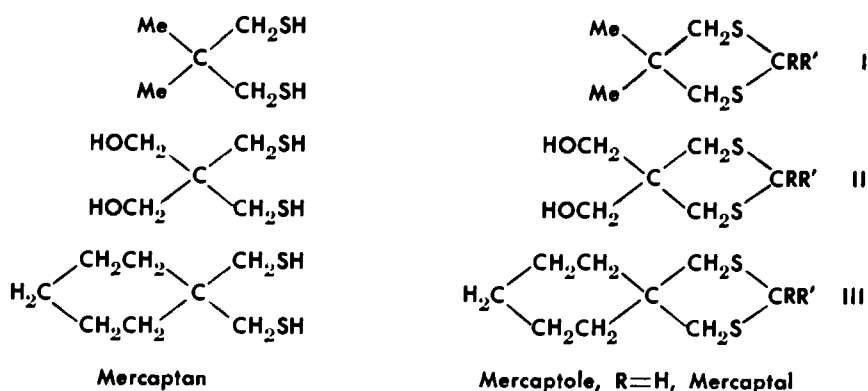
1,3-Dithiane has been prepared from formaldehyde and trimethylene mercaptan<sup>20b, 270</sup> and also from methylene chloride and trimethylene mercaptan in alkaline solution.<sup>458</sup> This mercaptan condenses readily with aldehydes and with ketones to give dithianes substituted in the 2-position,  $\text{RHC}(\text{SCH}_2)_2\text{CH}_2$  and  $\text{RR}'\text{C}(\text{SCH}_2)_2\text{CH}_2$ .<sup>19a, 20b, 143, 544</sup> The ultraviolet absorption of 1,3-dithianes has been studied.<sup>142</sup>

The formal of thioglycolic ester undergoes internal condensation in the presence of sodium ethylate:<sup>152</sup>

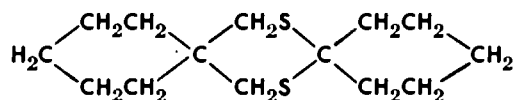


1,3-Dimercaptopropanol-2 gives a nearly quantitative yield of the mercaptal,  $\text{PhCH}(\text{SCH}_2)_2\text{CHOH}$ .<sup>649</sup> The reaction of  $\text{PhCOCH}:\text{C}(\text{SH})_2$  with trimethylene bromide results in the cyclic  $\text{PhCOCH}:\text{C}(\text{SCH}_2)_2\text{CH}_2$ .<sup>366a</sup> Propane-1,3-di-*p*-toluenethiolsulfonate with desoxybenzoin gives 2-benzoyl-2-phenyl-1,3-dithiane,  $\text{CH}_2(\text{CH}_2\text{S})_2\text{C}(\text{Ph})\text{COPh}$ ; with malonic ester the final product is 1,3-dithiane-2-carboxylic acid,  $\text{CH}_2(\text{CH}_2\text{S})_2\text{CHCO}_2\text{H}$ .<sup>158</sup> The isomer of this acid,  $\text{CH}_2(\text{SCH}_2)_2\text{CHCO}_2\text{H}$ , is from formaldehyde and 2-carboxytrimethylene mercaptan.<sup>352, 353</sup>

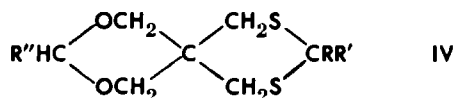
The mercaptans obtained by the action of sodium on the trimethylene disulfide derivatives, mentioned in a previous section, react well with aldehydes and ketones. The resulting mercaptals and mercaptoles are 1,3-dithianes:



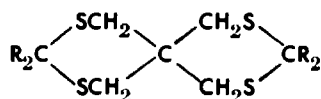
The mercaptan with the pentamethylene ring gives spiro compounds. The one from cyclohexanone would be a double spiro:



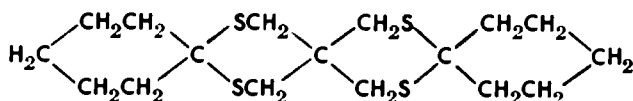
The mercaptan with the two hydroxyl groups reacts in two stages, the second giving a mixed compound:



Tetramercaptoneopentane,  $\text{C}(\text{CH}_2\text{SH})_4$ , reacts with aldehydes and ketones to give spiro-dithiolanes:

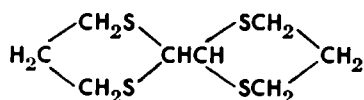


The compound from cyclohexanone contains four rings; as does the one from cyclopentanone: <sup>29c</sup>



Numerous derivatives of these are in the properties list.

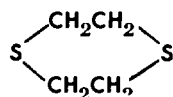
The reaction product of trimethylene mercaptan with 2,3-dichlorodioxane is probably the bis-mercaptal of glyoxal: <sup>545</sup>



With 1,4-diketohexamethylene,  $\text{OC}(\text{CH}_2\text{CH}_2)_2\text{CO}$ , a linear polymer is obtained.<sup>232</sup>

2,2-Dimethylsilico-1,3-dithiolane,  $b_2$   $54^\circ$ ,  $d$  20/4 1.1077,  $n$  20/D 1.5571, has been obtained from dimethylsilicon dichloride,  $\text{Me}_2\text{-SiCl}_2$ .<sup>570</sup>

### 1,4-Dithiane



Since 1,4-dithiane is the one of the three dithianes that is frequently encountered, the numerals are commonly omitted.

### Formation

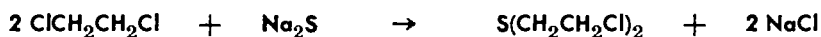
The first preparation of dithiane was by Löwig and Weidmann who treated ethylene chloride with potassium sulfide. In 1839 they could not have understood its structure.<sup>418</sup>

The reaction of ethylene bromide on sodium sulfide would be expected to give a high yield of dithiane since it is a six membered ring. As was mentioned in the introduction the product is a mixture of some dithiane and much of the linear polymer: <sup>172a, 172c, 445a, 453, 465a, 552d</sup>



The proportion of dithiane in the product varies according to the reaction conditions but is usually low. It was noted above that the speeds of formation of five, six, and seven membered sulfonium rings containing one sulfur atom are in the ratio of 6000:76:1. *n*-Pentane and sulfur give 2-methylthiophene, a five membered ring. Considering the large size of the sulfur atom the low yield of a six membered ring containing two sulfur atoms is not surprising.

The reaction of ethylene chloride and sodium sulfide cannot be stopped at the half way point even when the chloride is in large excess:

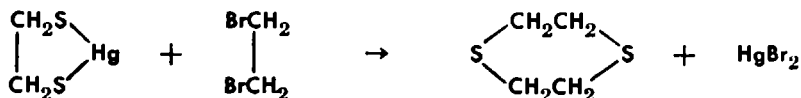


As was brought out more fully when mustard gas was discussed in Volume II, the halogen in the dichloro-sulfide is activated by

the sulfur atom in the  $\beta$ -position, to such an extent that this intermediate cannot survive.<sup>278</sup> In one experiment the mixture of ethylene chloride and sodium sulfide solution came in contact with the skin immediately after mixing and caused a slight burn showing the presence of a trace of the intermediate product.<sup>563</sup>

When a bromine atom is secondary or tertiary there may be dehydrohalogenation. Thus when 2,3-dibromobutane reacts with sodium sulfide 35% of it goes to butene-2 and only 16% to *s*-tetramethyldithiane. With isobutylene bromide these percentages are 41 and 13 and with 2-methyl-2,3-dibromobutane the yield of trimethylethylene is 69% and that of the cyclic compound zero.<sup>264</sup>

A metal derivative of ethylene mercaptan and ethylene bromide gives dithiane along with the polymer:<sup>344</sup>



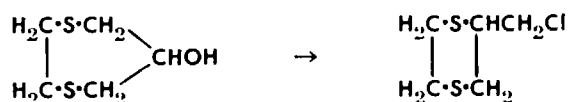
Dithiane can be prepared from ethylene mercaptan and ethylene bromide in alcohol solution in the presence of alkali. The more dilute the solution and the lower the reaction temperature the larger the proportion of dithiane in the product.<sup>344, 465a, 553b, 651</sup> The yield may be as high as 46%.<sup>671</sup>

The polymeric by-product which is always obtained in the preparation of dithiane can be converted into dithiane by heating to 160–80°. <sup>66, 172c, 344, 445a, 453, 458, 465a, 553b, 651, 671</sup> This statement does not seem to be true of a pure polymer of the composition  $(\text{CH}_2\text{CH}_2\text{S})_n$ <sup>66</sup> but is true of a polymer which contains halogen. It is difficult to remove all of the halogen.<sup>172c</sup> If the ethylene bromide is in excess the polymer should have bromine terminals,  $\text{BrCH}_2\text{CH}_2(\text{SCH}_2\text{CH}_2)_n\text{SCH}_2\text{CH}_2\text{Br}$ . The isolation of individual compounds in which  $n$  has values of from 9 to 47 has been claimed.<sup>553b</sup> The separation of the polymer into fractions of different average molecular weights is easy but to identify these as pure individual compounds is going too far. The decomposition of the polymer is well accounted for by assuming the formation and breaking up of sulfonium compounds.<sup>66</sup> The reactions which take place at the end of a polymeric molecule may be written:



of dithiane is formed when thiodiglycol is passed over heated alumina.<sup>721b</sup> Ethylene trithiocarbonate and ethylene bromide give dithiane,<sup>344</sup> so do methyl vinyl ethylene sulfide,  $\text{MeSCH}_2\text{-CH}_2\text{SCH:CH}_2$ , and ethyl iodide.<sup>105</sup> Dithiane has been found in the crude alcohol made by absorbing coke oven ethylene in sulfuric acid.<sup>666</sup> Dithiane may show up almost anywhere that  $\text{-CH}_2\text{CH}_2\text{-}$  and sulfur or its compounds are present. Some dithiane is found in the by-products from the preparation of ethylene mercaptan.<sup>72, 552a, 553a</sup> Mustard gas,  $\text{S(CH}_2\text{CH}_2\text{Cl)}_2$ , heated with a halogen compound, such as benzyl bromide, is converted to a derivative of dithiane.<sup>506</sup>

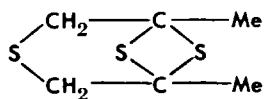
The tendency to the formation of the dithiane ring is shown by the contraction of a seven membered ring:



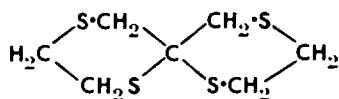
This occurs when the hydroxy derivative is heated with thionyl chloride. The formation of this 6-hydroxy-1,4-dithiacycloheptane from 2,3-dibromopropanol and ethanedithiol, instead of the expected six membered ring, seemed to violate this principle.<sup>259</sup> This may, however, be explained by assuming that the dibromohydrin was first changed to the epibromohydrin which should give the product that was actually obtained.

2,3,5,6-Tetramethyl-dithiane,  $\text{S(CHMe}\cdot\text{CHMe)}_2\text{S}$ , is formed when tetramethyldichloroethyl sulfide is heated with sodium sulfide.<sup>539</sup> 2,5-Dialkyl-dithianes result from the treatment of olefins with sulfur monochloride.<sup>274</sup>

Chloroacetone and hydrogen sulfide with hydrogen chloride give 2,6-dimethyl-(2,6-endosulfido)-1,4-dithiane: <sup>89, 90, 607a</sup>



Formerly this was thought to be trimeric thioacetone.<sup>112</sup> A double spirodithiane results when ethanedithiol reacts with dichloroacetone:

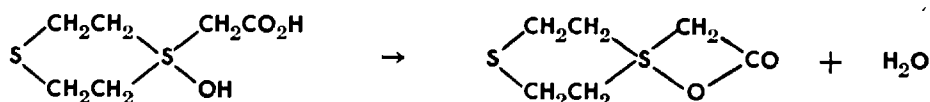


The analogous double spirothioxane is formed similarly from mercaptoethanol.<sup>35</sup>

### Reactions of Dithiane

Dithiane forms addition compounds with salts of the heavy metals, mercury,<sup>102, 344, 552b, 552c</sup> silver,<sup>102, 344</sup> cadmium, univalent and bivalent copper,<sup>102</sup> platinum,<sup>102, 344</sup> gold,<sup>344, 552b, 552c, 553a, 553c</sup> and iron.<sup>554</sup> Mercury may be determined by filtering off and weighing the precipitate,  $C_4H_8S_2 \cdot HgCl_2$ , which is formed in 0.2 N hydrochloric acid.<sup>609, 696</sup> A colored addition compound is formed with tetranitromethane.<sup>433</sup>

Dithiane takes up one or two molecules of methyl iodide to form sulfonium salts,<sup>105, 193, 281, 445b, 453, 506</sup>  $S(CH_2CH_2)_2SMeI$ , m.  $175^\circ$  and  $IMeS(CH_2CH_2)_2SMeI$ , m.  $208^\circ$ . The sulfonium hydroxide,  $S(CH_2CH_2)_2SMeOH$  loses a molecule of water and forms  $CH_2:CHSCH_2CH_2SCH_3$ .<sup>445b</sup> The velocity is proportional to the concentration of the two ions.<sup>281</sup> Dithiane combines with bromoacetic acid. The sulfonium bromide,  $S(CH_2CH_2)_2SCH_2CO_2HBr$ , melts at  $159^\circ$  and the chloride at  $167^\circ$ . The hydroxide loses a molecule of water:



Under other conditions the product is the isomeric,  $CH_2:CHSCH_2CH_2SCH_2CO_2H$ .<sup>651</sup> The addition of ethyl bromoacetate to dithiane is five times as rapid as to pentamethylene sulfide.<sup>159</sup>

Dithiane takes up bromine readily:



The product is hydrolyzed to the disulfoxide: <sup>172a, 344</sup>



The corresponding iodine compound,  $I_2S(CH_2CH_2)_2SI_2$ , a blue-black powder, containing 80.8% iodine, has antiseptic properties.<sup>24</sup>

Oxidation by ordinary nitric acid gives the disulfoxide while fuming takes it to the disulfone.<sup>172b</sup> There are two forms of the disulfoxide, one of which is five times as soluble as the other. They are believed to be *cis* and *trans*.<sup>65a, 70</sup> Further oxidation

gives the sulfoxide-sulfone,  $\text{OS}(\text{CH}_2\text{CH}_2)_2\text{SO}_2$ , m.  $279^\circ$ , and the disulfone,  $\text{O}_2\text{S}(\text{CH}_2\text{CH}_2)_2\text{SO}_2$ , m.  $> 330^\circ$ . The sulfoxide-sulfone can be reduced to the monosulfone, m.  $200^\circ$ .<sup>255</sup> The monosulfone is formed also by the addition of hydrogen sulfide to divinyl sulfone:<sup>6</sup>

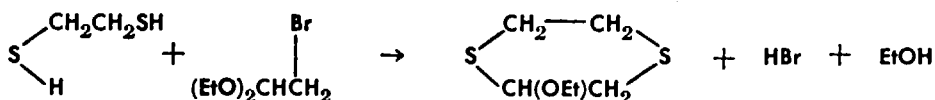


The dimethyl derivative of this,  $\text{O}_2\text{S}(\text{CH}_2\text{CHMe})_2\text{S}$ , is formed similarly from diallyl sulfone.<sup>31</sup> The reaction product of dithiane with chloramine-T is  $\text{MeC}_6\text{H}_4\text{SO}_2\text{N}:\text{S}(\text{CH}_2\text{CH}_2)_2\text{S}:\text{NSO}_2\text{C}_6\text{H}_4\text{CH}_3$ .<sup>441a</sup>

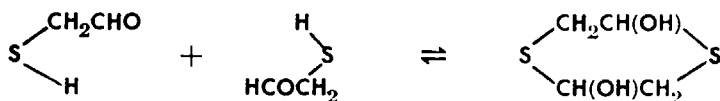
The ultra-violet,<sup>227b, 271, 336, 473, 474</sup> infra-red,<sup>221, 663</sup> and Raman spectra,<sup>157, 459, 663</sup> dipole moment,<sup>474</sup> and crystal structure<sup>198</sup> of dithiane have been investigated. The dipole moment is 0, indicating that it, like dioxane, is a flat molecule.<sup>134</sup> The vapor is in the "boat" form.<sup>312</sup> A staggered model is indicated with S—C distance 1.81 Å and C—C 1.54 Å. The S—C—C angle is  $111^\circ$  and the C—S—C  $100^\circ$ .<sup>314</sup>

### Derivatives of Dithiane

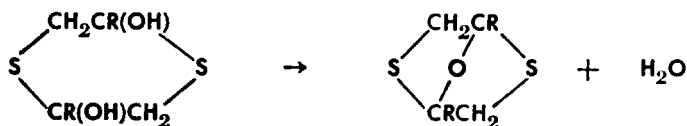
Ethanedithiol and bromoacetal react to form 2-ethoxydithiane:<sup>519</sup>



Mercaptoacetaldehyde exists in labile equilibrium with 2,5-dihydroxydithiane:<sup>321</sup>

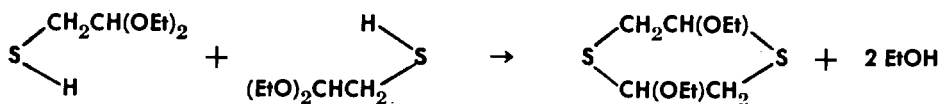


If instead of the aldehyde an  $\alpha$ -mercaptomethyl ketone is the starting material there will be alkyl,<sup>338, 660</sup> or aryl groups on the 2 and 5 carbons and the hydroxyls<sup>46, 284, 355</sup> will be tertiary. A molecule of water is lost leaving an endoxydithiane:



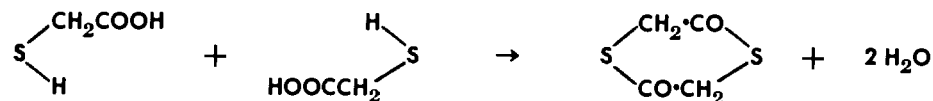


Thus the dehydration of dimeric acetonyl mercaptan gives 2,5-endoxy-2,5-dimethyldithiane.<sup>338, 660</sup> As will be seen later, the endoxy compounds are unstable intermediates on the way to dithiadienes and are seldom isolated. Their presence was not even suspected by some early workers. When  $\beta$ -mercaptoacetal is treated with acid, two molecules of it condense with the elimination of two of alcohol:



The product is 2,5-diethoxydithiane, a mixture of *cis* and *trans* forms.<sup>322, 525</sup>

Dithioglycolide, 2,5-diketo-dithiane, is formed when a current of dry air is passed through thioglycolic acid at 120° and the residue distilled in a vacuum:



It is hydrolyzed by alkali, the first product being  $\text{HSCH}_2\text{COSCH}_2\text{CO}_2\text{H}$ .<sup>593</sup> Its ketone nature is shown by the formation of bis-ketoles. That from thioglycolic acid is a tetrabasic acid, m. 204°, tetramethyl ester, m. 119.2°.<sup>592</sup>

Chloromethylsulfenyl chloride and acetoacetic ester give 2,5-diacetyl-2,5-carbethoxy-1,4-dithiane.<sup>111,7</sup> 1,3-Dimercaptoacetone is converted by a strong acid to 2,5-dihydroxy-2,5-bis(methylthiomethyl)-1,4-dithiane.<sup>607c</sup>

Dithiane-2,3-dicarboxylic acid is formed when dibromosuccinic acid reacts with ethylene mercaptan in alkaline solution. There are different forms according to whether the starting material is fumaric or maleic acid.<sup>48</sup> The ester of the isomeric 2,5-dicarboxylic acid has been made from ethyl  $\alpha,\beta$ -dibromopropionate and sodium sulfide.<sup>676</sup>

#### 1,4-Dithiene and 1,4-Dithiadene



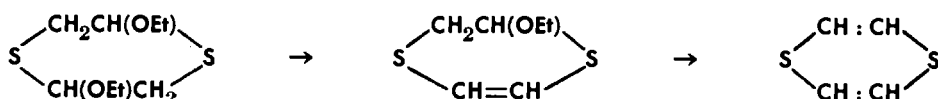
Back in 1890 Levi<sup>410</sup> obtained an oil, b. 167–70°, by treating thioglycolic acid with phosphorus trisulfide. This he called

biophene and, on the basis of a sulfur analysis, gave it the structure of 1,4-dithiadene. He prepared acetyl and benzoyl derivatives from it by the Friedel-Crafts reaction. Just what he had remains a mystery as attempts to repeat it have been unsuccessful.<sup>338, 525</sup>

### Formation

A small yield of 2,5-dicarbethoxymethyldithiadene has been obtained by treating  $\beta$ -acetylmercaptoacetoacetic ester with sulfuric acid and also from  $\beta$ -bromoacetic ester and sodium hydrosulfide.<sup>643</sup>

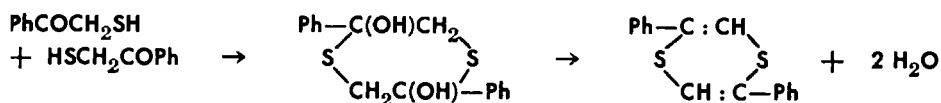
Recently dithiadene itself has been prepared and thoroughly investigated. A molecule of ethanol can be split off from 2-ethoxydithiane leaving 1,4-dithiene.<sup>519</sup> When 2,5-diethoxydithiane is passed over alumina at 300° it loses ethanol in two stages:



At 110° phosphorus pentoxide abstracts only one molecule of alcohol.<sup>525</sup>

From x-ray diffraction it has been concluded that the unit cell is orthorhombic and that the molecule has the "boat" configuration with an angle of 137° between the planes.<sup>524</sup>

2,5-Diphenyldithiadene was first obtained from a substituted pyrimidine.<sup>355</sup> It is prepared most conveniently from phenacyl mercaptan:<sup>284</sup>



It is unnecessary to prepare the mercaptan as such. A  $\beta$ -keto-halide is made to react with sodium thiosulfate and the resulting Bunte salt is treated with excess hydrochloric acid which condenses the keto-mercaptan as it is liberated. This is a general method and the yields are good.<sup>46</sup> The same compound can be obtained from 1-chloro-1-phenylacetone by treating it with carbon disulfide and hydrogen chloride.<sup>89</sup>

### Reactions

The oxidation of 1,4-dithiadene takes place in two steps, to the monosulfone, m. 100°, and to the disulfone, m. 242.5°.<sup>525</sup>

The oxidation of the 2,5-diphenyl derivative is complicated. A bicyclic intermediate has been isolated. The final products are 50% of the disulfone and benzoic acid, besides sulfuric acid.<sup>556</sup>

Contrary to the reported properties of Levi's compound dithiadiene appears to be aliphatic.<sup>524</sup> However, aromatic characteristics are shown by its 2,5-diphenyl derivative. This is nitrated readily, the nitro group entering the 3-position of the dithiadiene ring. Oxidation of the product gives benzoic acid, but no nitrobenzoic. Milder oxidation gives two isomeric monosulfones.<sup>523</sup>

When 2,5-diphenyl-1,4-dithiadiene is heated to 190° an exothermic reaction occurs and the temperature goes to 250°. The products are sulfur and the more stable 2,4-diphenyl-thiophene. This is formed also in the thermal decomposition of the monosulfone. In this case the other product is sulfur dioxide. The 6-nitro-2,5-diphenyl-1,4-dithiadiene mentioned above decomposes in the same way. The reaction starts at 135° and 5-nitro-2,4-diphenylthiophene is formed.<sup>523</sup> An attempt was made to introduce the formyl group by means of dimethylformamide and phosphorus oxychloride. The product was 5-formyl-2,4-diphenylthiophene.<sup>523</sup>

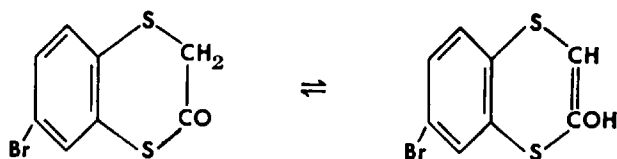
### Benzodithiene and Benzodithiadiene

The synthesis of these was accomplished by a series of reactions analogous to those described above for 1,4-dithiadiene. The reaction product of a molecule of diethyl 2-bromoacetal with one of dithiocatechol in alkaline solution was condensed by hydrogen chloride to 2-ethoxybenzo-1,4-dithiene. Treatment of this with phosphorus pentoxide leaves benzo-1,4-dithiadiene. This is a stable, pale yellow-green oil,  $b_{0.1}$  67–70° and, under nitrogen, at 220° at normal pressure. It fluoresces a brilliant green in ultraviolet light. It was characterized by its ultraviolet spectrum and by its addition compound with trinitrobenzene.<sup>522, 576</sup> The assumed structure has been verified in two ways. The compound was oxidised to the disulfone which was hydrogenated. Dithiocatechol and ethylene bromide reacted in alkaline solution to give benzo-1,4-dithiene which was oxidised to the disulfone which proved to be identical with the other sulfone. The benzo-1,4-dithiene was dehydrogenated by chloranil to benzo-1,4-dithiadiene.<sup>522, 576</sup>

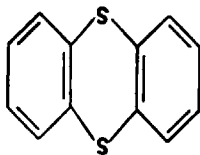
Formylation by a standard procedure gave the aldehyde with

no splitting out of sulfur. This was oxidised to the acid.<sup>522</sup> Acetylation was accomplished with acetanhydride and 85% phosphoric acid. Mild oxidation of this gave the above carboxylic acid. That these groups are in the dithiadene ring was proved by drastic oxidation which gave *o*-benzenedisulfonic acid. This was obtained also by the oxidation of the nitro derivative. Thus the aromatic character of the dithiadene ring was demonstrated. Substitution takes place in it even more readily than in the adjoining benzene ring.<sup>524</sup>

The reaction of chloroacetic acid with 4-bromodithiocatechol gives a thiolactone which, in its enol form, can be regarded as a hydroxybenzodithiadene:<sup>288</sup>



Thianthrene



Thianthrene, dibenzodithiadene, follows logically but is only mentioned here.

#### 1,4-Diselenane

This was first prepared from  $\beta,\beta'$ -dichloroethyl selenide and lithium selenide<sup>279</sup> but later from aluminum selenide and ethylene bromide.<sup>438</sup> From the x-ray study of the crystals the C—Se bond appears to be longer than was expected.<sup>450</sup> It takes up halogens to form a tetrachloride, m. 178–81°, a tetrabromide, m. 148–51°, and a tetraiodide, m. 151°.<sup>438</sup>

#### FIVE CARBON AND TWO SULFUR ATOMS

From  $\alpha,\alpha'$ -dibromopimelic acid and sodium polysulfide 1,2-dithiacycloheptane-3,7-dicarboxylic acid has been obtained along with some of the corresponding monosulfide.<sup>607d</sup> The 4,8-thioctic acid, which was synthesized in determining the structure of lipoic acid, is 3-( $\beta$ -carboxyethyl)-1,2-dithiacycloheptane.<sup>126, 127</sup>

1,4-Dithiaheptane<sup>20b, 458, 671</sup> and its 6-hydroxy derivative<sup>259</sup> have been synthesized by conventional methods.

### LARGER RINGS WITH TWO SULFUR ATOMS

The formation of rings of various sizes from aliphatic dimercaptans and  $\alpha,\omega$ -dihalides has been discussed in the introduction of this chapter. Here attention is directed to a few examples involving aromatic dimercaptans.

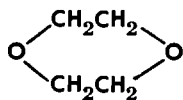
Xylene dimercaptans,  $C_6H_4(CH_2SH)_2$ , both ortho and meta, have been used in making cyclic compounds. In preparing the dimercaptan from *o*-xylene dibromide and potassium hydrosulfide the by-product was the dimeric sulfide,  $C_6H_4(CH_2SCH_2)_2-C_6H_4$  instead of  $C_6H_4(CH_2)_2S$ , the five membered ring which might have been expected. The preparation of the monomeric sulfide has been mentioned above. Two mercaptals from *o*-xylene dimercaptan,  $C_6H_4(CH_2S)_2CH_2$  and  $C_6H_4(CH_2S)_2CHMe$ , and a mercaptole,  $C_6H_4(CH_2S)_2CMePh$ , have been prepared. These rings have seven members.<sup>19b</sup>

The mercaptole from pentamethylene mercaptan and acetone turned out to be the dimer,  $H_2C(CH_2CH_2\cdot S\cdot CMe_2\cdot S\cdot CH_2CH_2)_2-CH_2$ .<sup>18</sup> The reaction of *m*-xylene dimercaptan with acetone and *p*-xylene dimercaptan with benzaldehyde gave the 16 and 18 membered mercaptoles, *m*- $C_6H_4(CH_2SC(Me_2)SCH_2)_2C_6H_4$  and *p*- $C_6H_4(CH_2SCHPhSCH_2)_2C_6H_4$ , instead of 8 and 9 membered rings.<sup>17</sup> From *m*-xylene dibromide and dithioresorcinol, *m*- $C_6H_4(SH)_2$ , the 20-membered ring *m*- $C_6H_4(SCH_2C_6H_4CH_2S)_2C_6H_4$ , is obtained instead of the ten-membered.<sup>565</sup>

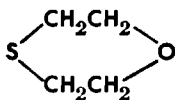
2,2'-Dimercaptobiphenyl gives seven membered mercaptals and mercaptoles with aldehydes and ketones.<sup>51</sup>

### THIOXANE

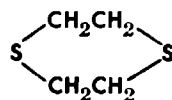
Thioxane, or oxathiane,  $S(CH_2CH_2)_2O$ , may be taken up at this point. It occupies an intermediate place between dioxane and dithiane:



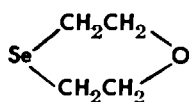
b. 101.4°  
m. 13.0°



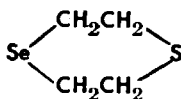
b. 148.7°  
m. -17°



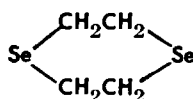
b<sub>80</sub> 115.6°  
m. 113°



b<sub>348</sub> 156.6°<sup>354</sup>  
m. -21.5°



b<sub>97</sub> 86.5°  
m. 107°<sup>269</sup>



m. 113.5°<sup>438</sup>

The boiling point of thioxane is approximately the average of those of dioxane and dithiane but the melting point is below that of either. This is to be expected on account of its lower symmetry. Three selenium compounds are added for comparison.<sup>269, 354, 438</sup>

Thioxane was first made from 2,2'-diiodoethyl ether and potassium sulfide.<sup>159</sup> It is easily prepared. To 2500 cc. of a 2 molar solution of sodium sulfide containing about 1 g. of a dispersing agent, such as a sodium alkyl naphthalenesulfonate, and 16 g. of sodium hydroxide, a solution of 40 g. hydrated magnesium chloride is added slowly with stirring. This mixture is heated to about 70° and 572 g. (4 moles) of dichloroethyl ether added dropwise, with stirring, at such a rate that the temperature keeps around 90 to 95°. External cooling may be used. When after two or three hours the temperature begins to drop, heat is applied and the mixture refluxed for half an hour. The thioxane is distilled out with steam. The crude thioxane should be refluxed with a solution of sodium sulfide or polysulfide to free it from traces of unreacted dichloroether. It is then purified by fractionation.

A mixture of thioxane and water boils at 96° and the distillate is one part thioxane to two of water. The thioxane layer contains about 1% of water, and the water layer about 7% of thioxane. This is best recovered by steam-distilling the water layer.<sup>182</sup>

In the preparation of thioxane no appreciable amount of polymer is formed. The tendency to form thioxane is so great that 16% of it is produced even when sodium tetrasulfide is substituted for the sulfide. It is then accompanied by the expected linear polymer having the unit  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}_4-$ .<sup>527</sup> Thioxane is formed when ethylene oxide,<sup>721a</sup> or glycol,<sup>722</sup> and hydrogen sulfide are passed over alumina at 200–25°, or when thiodiglycol is distilled over potassium bisulfate.<sup>255, 721b</sup>

The alkaline hydrolysis of 2,2'-dichlorodiethylsulfoxide,  $\text{OS}(\text{CH}_2\text{CH}_2\text{Cl})_2$ , and the sulfone,  $\text{O}_2\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2$ , yield the sulfide and sulfone of thioxane.<sup>6, 148</sup>

The 3,5-dimethyl derivative,  $\text{S}(\text{CH}_2\text{CHMe})_2\text{O}$ , is from dichloro-*i*-propyl ether and sodium sulfide.<sup>340</sup> The tetramethyl

derivative is formed by the addition of hydrogen sulfide to methallyl ether: <sup>298</sup>



A similar addition takes place with diallyl amine:



Thioxane takes up iodine, bromine, or ethyl iodide. The products are:  $\text{I}_2\text{S}(\text{CH}_2\text{CH}_2)_2\text{O}$ , m.  $67^\circ$ , <sup>255</sup>  $\text{Br}_2\text{S}(\text{CH}_2\text{CH}_2)_2\text{O}$ , m.  $85^\circ$ , <sup>182</sup>  $\text{IEtS}(\text{CH}_2\text{CH}_2)_2\text{O}$ , m.  $85^\circ$ . <sup>255</sup> It can be oxidised to the sulfoxide,  $\text{OS}(\text{CH}_2\text{CH}_2)_2\text{O}$ , and sulfone,  $\text{O}_2\text{S}(\text{CH}_2\text{CH}_2)_2\text{O}$ . The sulfoxide reacts with hydriodic acid: <sup>255</sup>



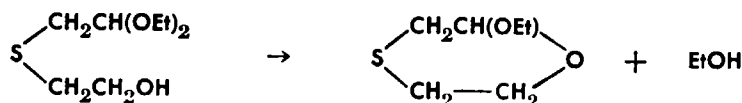
The mercuric chloride addition product melts at  $174^\circ$ . <sup>182</sup> Thioxane is oxidised to the sulfoxide by hydrogen peroxide at  $70\text{--}100^\circ$ . <sup>632</sup> The sulfone is produced by the alkaline hydrolysis of the disulfone from dithiane. <sup>62</sup> It is formed also when 2-hydroxy-2'-ethoxy-diethyl sulfone is distilled: <sup>391</sup>



The sulfoxide and the sulfone are formed also by addition of water to vinyl sulfoxide and sulfone. <sup>6</sup> Thioxane forms addition products with sulfur trioxide and with chlorosulfonic acid. <sup>503</sup>

The dipole moment of thioxane is  $0.47$ . <sup>88</sup> Its light absorption <sup>271, 336</sup> and Raman spectrum <sup>227b, 459</sup> have been studied.

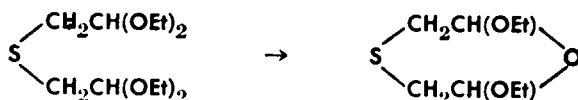
$\beta$ -Hydroxyethylmercaptoacetic acid,  $\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{COOH}$ , loses a molecule of water. The product, which is insoluble in acid and in alkali, may be the lactone or a linear polymer. <sup>568</sup> 2-(2-Hydroxyethylmercapto)acetal, in the presence of acid, goes to 3-ethoxythioxane: <sup>517</sup>



This is an acetal and, in dilute hydrochloric acid solution, is in equilibrium with ethyl alcohol and the aldehyde,  $\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CHO}$ , from which the usual aldehyde derivatives can be obtained. Methoxyl <sup>518, 519</sup> and butoxyl <sup>517</sup> derivatives are similar, both as to methods of preparation and reactions. The 3,3-di-

methyl-5-ethoxy-<sup>517</sup> and the 2,3-dimethyl-3-ethoxy-dithioxanes<sup>519</sup> have been prepared similarly.

The 3,5-diethoxy derivative of thioxane is formed when the sulfide of acetal is treated with hydrogen chloride:<sup>180</sup>

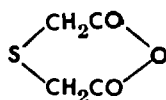


By dilute acid the same sulfide is converted into the 3,5-dihydroxy derivative which seems to be in equilibrium with the aldehyde sulfide:



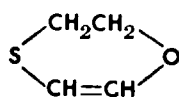
The 3,5-dihydroxythioxane reacts with alcohol to give the 3,5-diethoxythioxane.

The 3,5-dicarboxylic acid is from the hydrolysis of the dinitrile which, in turn, is formed by the addition of hydrocyanic acid to the aldehyde.<sup>164</sup> The anhydride of thioglycollic acid may be considered to be 3,5-diketothioxane:<sup>7,5</sup>

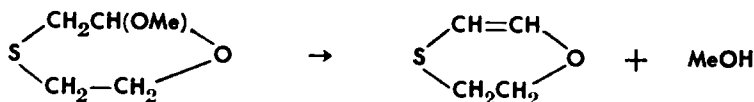


Its 2,6-dimethyl- and 2,6-diethyl derivatives have been made.<sup>394,5</sup>

#### 1,4-THIOXENE



The story here runs parallel to that for 1,4-dithiene. The starting material is an alkoxythioxane, the preparation of which was described in the preceding section. Methanol is eliminated from 3-methoxythioxane by heating it with a catalytic amount of phosphorus pentoxide:<sup>518</sup>

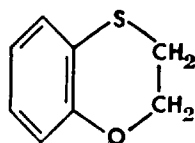


1,4-Thioxene appears to be stable when kept free of peroxides. It polymerizes to a solid which melts over the range 200 to 220°. In the presence of an acid catalyst it takes up methanol to form



the methoxythioxane, reversing the above reaction.<sup>518</sup> A mixture of 2-methoxythioxane and the thioxene is obtained when the chloroacetal is heated with mercaptoethanol in carbon disulfide or without solvent. The same is true of the 2,5-dimethyl compounds.<sup>519</sup>

### *Benzothioxene*



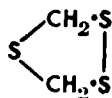
Monothiocatechol and  $\beta$ -bromomercaptal react to give 3-ethoxybenzothioxene. As this is an acetal the ethoxy group can be exchanged for another alkoxy or hydroxyl group by treating it with acid in an alcohol or in water. The hydroxy compound can be acetylated. The 3-ethoxy compound loses a molecule of alcohol to form benzothioxadiene when its vapor is passed over phosphorus pentoxide at 300°.<sup>520</sup>

### *Benzo-1,4-thioxadiene*

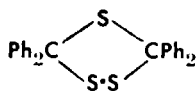
This is prepared by reactions analogous to those used for benzo-1,4-dithiadiene. The starting materials are diethyl bromoacetal and monothiocatechol. The elimination of the ethanol from the intermediate 2-ethoxy compound has proved to be more difficult than from the corresponding disulfur compound. Dehydration of the hydroxy and deacetylation of the acetyl derivative give benzo-1,4-thioxadiene identical with that from the 2-ethoxy. The addition of bromine to benzo-1,4-thioxadiene gives a stable dibromide, hydrolysis of which yields glyoxal. Formylation introduces the aldehyde group which indicates the aromatic character of the diene ring. Oxidation gave the sulfone of benzo-1,4-thioxadiene which was hydrogenated. This proved to be identical with the sulfone from benzo-1,4-thioxene prepared from monothiocatechol and ethylene bromide.<sup>520</sup>

## **Rings Containing Three Sulfur Atoms**

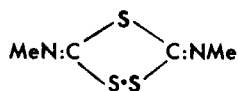
### **TWO CARBON AND THREE SULFUR ATOMS**



By the auto-oxidation of thiobenzophenone a trisulfide having the composition  $(\text{Ph}_2\text{C})_2\text{S}_3$  has been obtained. This has been shown to have the structure I.<sup>141, 358, 602, 639</sup> By a series of reactions, starting with methylisothiocyanate, a compound II has been prepared.<sup>241, 242</sup>



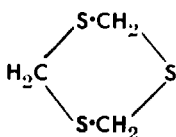
I



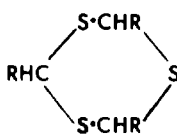
II

### THREE CARBON AND THREE SULFUR ATOMS

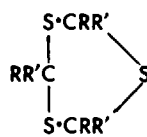
#### Trithiane



Trithioformaldehyde



Trithioaldehyde

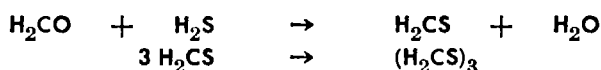


Trithioketone

#### General

Trithioformaldehyde is trithiane; the trithioaldehydes and trithioketones are its symmetrical alkyl or aryl derivatives.

Trithiane is the product often isolated when reactions are carried out that should give monomeric thioformaldehyde:



Thioaldehydes and the simpler thioketones trimerize similarly at the moment of formation. The tendency to trimerize is far stronger with these sulfur compounds than with their oxygen analogs. In only a few cases, practically all of which are aromatic, can monomeric thioaldehydes or thioketones be isolated. Among the oxygen compounds only the lower aliphatic aldehydes trimerize readily; trimeric ketones are unknown. The true cyclic trioxymethylene, the analog of trithiane, can be made but formaldehyde usually appears as an amorphous linear polymer.

The preparation of trithiane is taken up in chapter 2 on Thials and Thiones.

Trithiane is an odorless solid, melting at  $216^\circ$ , only slightly soluble in hot water, more so in hot alcohol and ether. The trimeric formula,  $(\text{H}_2\text{CS})_3$ , has been verified by vapor density

measurements and freezing point determinations on its solutions.<sup>59b</sup> It is orthorhombic; the dimensions of the unit cell are 7.63, 7.00, and 5.25 Å.<sup>472</sup> The Raman spectrum<sup>227b, 382</sup> and ultra-violet absorption have been studied.<sup>194</sup> The dipole moment is 2.3, indicating a chain configuration or a mobile equilibrium in which this form predominates.<sup>134</sup> Trithiane has a staggered form. The S—C distance is 1.81 Å, the S—S 3.05 Å. The C—S—C angle is 114.5°, the S—C—S, 106.5°.<sup>314</sup>

The trithiane obtained by early chemists,<sup>342, 414</sup> in extremely small yield, by passing hydrogen sulfide over hot lead formate must have been impure. For that reason its properties are disregarded here.

According to the structural formulae at the top of this section, the cyclic trimers of the higher thioaldehydes and of unsymmetrical ketones should be capable of existing in cis and trans forms. With trithioformaldehyde and with compounds from symmetrical ketones there is not this possibility. The supposed isolation of an isomeric form melting at 247° led to the invention of a sulfur atom with two valence centers and to much controversy.<sup>153a, 153b, 253, 254, 323a, 324a, 324b, 324c, 324d</sup>

The analogous selenium compound, (CH<sub>2</sub>Se)<sub>3</sub>, 1,3,5-triselenacyclohexane, is formed from formaldehyde and hydrogen selenide. Chlorination of this gives (ClCH<sub>2</sub>)<sub>2</sub>Se, ClCH<sub>2</sub>SeCl, and (ClCH<sub>2</sub>-Se)<sub>2</sub>.<sup>111</sup>

### Oxidation of Trithiane

As each of the three sulfur atoms in trithiane can be oxidised in two steps a number of oxidation products are possible.<sup>56a, 57, 144, 323a, 324a, 533</sup> Its planar ring structure was beautifully demonstrated by the preparation of all of the possible sulfoxides. The oxidation of trithiane in acetone by hydrogen peroxide gave a monosulfoxide, m. 187°. Further oxidation produced a mixture of two disulfoxides, A and B, having quite different solubilities. According to theory there should be two disulfoxides, a cis and a trans, which should differ in solubilities. Further oxidation of A gave two trisulfoxides. From this it was concluded that A is the cis form. Starting with the two oxygens on the same side of the plane of the ring, the addition of a third oxygen should give two trisulfoxides, the one having all of the three oxygens on the same side of the plane and the other, a cis-trans, having the third

oxygen on the other side. The form B which was assumed to be trans should give only one trisulfoxide, identical with one of those from A. This was found to be the case.<sup>65b</sup> The final oxidation product of all of these is the trisulfone.

Oxidation by permanganate may lead to the sulfonic acid salts,  $S(CH_2SO_3K)_2$ ,  $O_2S(CH_2SO_3K)_2$  and  $H_2C(SO_3K)_2$ .<sup>345</sup>

The trisulfone is extremely stable and sublimes without melting. It is acidic enough to form salts,  $C_3S_3O_6H_5Na \cdot H_2O$ ,  $(C_3S_3O_6H_5)_2Ba \cdot 4H_2O$ . If it is dissolved in excess of 10% sodium hydroxide, plus an equal volume of alcohol, and an excess of methyl iodide is added the liquid will be filled the next day with inch long needles of the hexamethyl derivative, m.  $302^\circ$ , identical with the trisulfone from trithioacetone.<sup>57, 144</sup> With ethyl iodide the reaction is slower and incomplete.<sup>144</sup>

Bromination gives two products: <sup>56a, 533</sup>



#### Addition Compounds with Metal Salts

A characteristic reaction of alkyl sulfides is the formation of complexes with metal salts,  $R_2S \cdot HgCl_2$ , etc. These complexes contain one, or sometimes two, molecules of the mercury salt for each sulfur atom. The same can be said of the complexes with other heavy metal salts, such as platinum and gold. It is curious that trithiane, which is a triple sulfide, combines with only one molecule of a metal salt as in  $C_3H_6S_3 \cdot AgNO_3$  and  $C_3H_6S_3 \cdot PtCl_4$ . This fact was used by early investigators to prove the trimeric formulae for thioformaldehyde and thioacetaldehyde.<sup>272, 327c, 327d, 374c, 446a</sup> Trithioformaldehyde forms complexes also with aluminum salts.<sup>403a</sup> Its compound with perchloric acid,  $(C_3H_6S_3)_3 \cdot (HClO_4)_2$ , acts like a true salt.<sup>324c</sup>

#### Other Reactions

Chlorine converts trithiane to  $ClCH_2SCHCl_2$ ,<sup>273</sup> or to  $ClCH_2SO_2Cl$ ,<sup>111.3, 385, 403b</sup> according to conditions. Chlorination in cold carbon tetrachloride gives chloromethanesulfonyl chloride which is taken up in chapter 3, Volume I.<sup>201</sup> The same is true of the substituted trithianes.<sup>200</sup> Chlorination of trithianes forming substituted sulfides is in chapter 5, Volume II.

The cautious addition of sulfur monochloride to cold trithioformaldehyde gives dichlorodimethyl sulfide,  $\text{ClCH}_2\text{SCH}_2\text{Cl}$ .<sup>86, 441b</sup>

When trithiane and dimethyl sulfate are heated on the water bath for several hours and potassium iodide is added the monomethiodide is obtained. The ethiodide is made similarly.<sup>403a</sup> When it is heated to  $100^\circ$  in a sealed tube with methyl iodide and methanol it undergoes complete cleavage:<sup>569</sup>



Useful products resulting from the condensation of thioformaldehyde with urea have been claimed.<sup>217, 447, 448, 535</sup> Trithioformaldehyde is useful in tanning<sup>471</sup> and in flotation.<sup>400</sup> Hydrogen sulfide may be reacted with an excess of formaldehyde and the product condensed with phenol and urea or other nitrogen compounds.<sup>218</sup>

### *Trithioacetaldehyde*

The preparation of trimethyltrithiane, or trithioacetaldehyde, will be given in chapter 2 on Thials and Thiones. Here it will be considered as a cyclic sulfide in relation to other cyclic sulfides.

The cyclic formula for trithioacetaldehyde accounts for cis and trans forms. The crude product has been found to be a mixture of two substances having the same composition but differing in melting points  $\alpha$   $101^\circ$ ,  $\beta$   $125^\circ$ , and in other characteristics.<sup>56b, 59a, 59b, 153a, 246a, 374a, 374c, 374d, 655, 706</sup> The  $\alpha$ -form is monoclinic and the  $\beta$ -orthorhombic.<sup>67</sup> The molecular weights of both correspond to the trimeric formula.<sup>59b</sup> The densities are  $\alpha$ -d 20/4 1.178,  $\beta$ -d 20/4 1.150.<sup>21</sup> Infrared absorption spectra indicate that paraldehyde and the two forms of trithioacetaldehyde have the same ring structure<sup>266</sup> which is of the symmetrical staggered, cyclohexane type. The C—S—C angle is  $106.5^\circ$  and the S—C—S angle  $114.5^\circ$ .<sup>313</sup> The cis structure has been assigned to the  $\alpha$ -form, m.  $101^\circ$ , and the trans to the  $\beta$ -form, m.  $125^\circ$ ,<sup>59a</sup> though the Raman spectra seem to show that it should be the other way.<sup>265</sup> It has been found that the one can be converted to the other by certain catalysts.<sup>312, 374a, 374c, 374d, 441b, 441c, 446c, 655</sup> To explain isomerism it has been suggested that the three sulfur and the three carbon atoms may not lie in a plane.<sup>138, 595b</sup> The configurations of the two forms have been studied.<sup>312</sup>

A third, or  $\gamma$ -form of trithioacetaldehyde, melting at  $76^\circ$  or  $81^\circ$ , and not accounted for by theory, plagued chemists for 40 years,<sup>58b, 59d, 203, 441b, 441c, 446c, 537</sup> until it was shown to be a mixture of the two other forms.<sup>58b, 59d, 67, 248</sup>

Trithioacetaldehyde forms an addition product with silver nitrate.<sup>689</sup>

Oxidation of trithioacetaldehyde gives a variety of products,  $C_6H_{12}S_3O$ ,  $C_6H_{12}S_3O_2$ ,  $C_6H_{12}S_3O_3$ ,  $C_6H_{12}S_3O_4$ ,  $C_6H_{12}S_3O_5$ , and  $C_6H_{12}S_3O_6$  according to the reagents used and the conditions.<sup>56b, 248, 286a, 286e</sup> The disulfoxide melts at  $255^\circ$  with decomposition,<sup>248</sup> the  $\alpha$  trisulfoxide m.  $184^\circ$ , and the  $\beta$ -isomer at  $153^\circ$ .<sup>248</sup> Both  $\alpha$ - and  $\beta$ -modifications of trithioacetaldehyde give the same disulfone-sulfide, m.  $284^\circ$ .<sup>56b</sup> With permanganate, the sulfonic acid salt,  $CH_3CH(SO_3K)_2$ , is obtained.<sup>286a, 286e</sup> Oxidation of the  $\beta$ -form by hydrogen peroxide gives a mono-sulfoxide, m.  $118.5^\circ$ , with permanganate, a mono-sulfone, m.  $190^\circ$ . Oxidation of the  $\alpha$ -form leads to two mono-sulfoxides,  $\alpha$ -m.  $136^\circ$  and  $\beta$ -m.  $93^\circ$ , and then to two mono-sulfones melting at  $157.5^\circ$  and  $116^\circ$ . From this it has been concluded that the  $\alpha$ -form has the *trans* configuration and the  $\beta$ -form the *cis*.<sup>153a</sup> Alkylation of the trisulfone with methyl iodide and alkali gives triacetone sulfone.<sup>58b, 420</sup> The trisulfone is sufficiently acidic to form stable sodium, potassium, barium, strontium, and silver salts.<sup>420</sup>

Trithioacetaldehyde is desulfurized by copper to butene-2.<sup>210</sup> Electrolysis in hydrochloric acid solution leads to  $(CH_3CClS)_3$ .<sup>229</sup> Chlorination gives the chlorosulfone chloride,  $CH_3CHClSO_2Cl$ .<sup>499</sup> At low temperature the sulfenyl chloride,  $CH_3CHClSCl$ , is formed.<sup>200</sup>

On long standing with methyl iodide trimethyl sulfonium iodide was produced and with ethyl iodide, triethyl sulfonium iodide.<sup>536</sup> Trimethyl sulfonium iodide decomposes at  $215^\circ$  without melting.<sup>374b</sup> Heating trithioacetaldehyde in a sealed tube with hydriodic acid gives ethyl disulfide.<sup>95</sup> If an alcoholic solution of trithioacetaldehyde is added to a fermenting aqueous sugar solution ethyl mercaptan is formed.<sup>507, 508</sup>

### Other Trithioaldehydes

Chloral reacts normally giving *tris*-trichlormethyl trithiane.<sup>153c</sup> Trithiopropionaldehyde,<sup>200, 203</sup> trithio-*i*-butyraldehyde,<sup>203</sup> and tri-

thiovaleraldehyde<sup>200</sup> have been prepared but little is known about them.

Thioaldehydes are said to be useful in flotation.<sup>400, 580</sup>

Tetraethenyl hexasulfide,  $(\text{MeC})_4\text{S}_6$ , has been known for some time but its structure has been determined only recently. It consists of four trithiane rings in which each sulfur atom is common to two rings. Its structure is analogous to that of hexamethylene-tetramine.<sup>96, 145, 239d, 251</sup> It is one of the products from acetyl chloride and hydrogen sulfide in a sealed tube. Its molecular weight was found to be around 270 instead of the calculated 296.<sup>99</sup> It is orthorhombic and crystallizes from acetic acid as six-fold twins.<sup>196</sup>

### *Aromatic Trithioaldehydes*

Trithiobenzaldehyde, which may be called *s*-triphenyl-trithiane, is readily prepared from benzaldehyde, hydrochloric acid, and hydrogen sulfide. Ammonium sulfide was used with benzaldehyde in an old preparation.<sup>397</sup> Several have made it from benzal chloride and alkali sulfide.<sup>63, 132a, 252</sup> Its preparation will be discussed more fully in chapter 2 on Thials and Thiones.

Two forms are known,  $\alpha$ - and  $\beta$ -, melting at 167° and 226°, respectively. A supposed third form bothered chemists for a time but was shown to be a mixture of the other two.<sup>58b, 655</sup> This was rediscovered later<sup>323b</sup> but was again discredited.<sup>253</sup> Molecular weight determinations show that both forms have the molecular weight corresponding to the trimer,  $(\text{PhCHS})_3$ .<sup>59b</sup> The dipole moments of the two forms are almost identical, 2.09 and 2.08. These do not agree with the values calculated for the boat and chair forms.<sup>319</sup>

Trithiobenzaldehyde has been oxidised to the trisulfoxide and trisulfone. The latter can be alkylated with methyl iodide and alkali but only two methyl groups can be introduced. This has been attributed to steric hindrance.<sup>253</sup> Chlorination at low temperature gives the sulphenyl chloride,  $\text{PhCHClSCl}$ .<sup>200</sup> Trithiobenzaldehyde is desulfurized to stilbene by copper powder.<sup>374a, 374b</sup> It has been used with thiourea for making plastics.<sup>535</sup>

*o*-Trihydroxytrithiobenzaldehyde has been prepared by the hydrogen sulfide-hydrogen chloride method. A chlorine derivative has been claimed as a fungicide.<sup>587</sup> Trithiophenylacetaldehyde,  $(\text{PhCH}_2\text{CHS})_3$ , has been prepared by the same method.<sup>199</sup>

*Trithioketones*

## Trithioacetone, Hexamethyltrithiane

Acetone and hydrogen sulfide react, in the presence of hydrochloric acid, to give trithioacetone:



Only the trimeric form can be isolated but enough of the monomer escapes in the preparation to cause trouble with the odor which is said to surpass all others in intensity.<sup>58a</sup> The molecular weight corresponds to the trimer. It is formed also in the thermal decomposition of the mercaptole from acetone,  $\text{Me}_2\text{C}(\text{SEt})_2$ , and of the thioacetic acid mercaptole,  $\text{Me}_2\text{C}(\text{SCOMe})_2$ .<sup>635a</sup> It has been prepared from acetone by treating it with carbon disulfide and zinc chloride<sup>89</sup> or with magnesium bromsulfhydrate,  $\text{Br}\cdot\text{MgSH}$ .<sup>469</sup>

Theory calls for but one form, and only one has been found.<sup>253</sup>

Trithioacetone can be oxidised to a disulfone, m.  $208^\circ$ ,<sup>58a</sup> or a trisulfone, m.  $302^\circ$ .<sup>58a, 469</sup> Chlorination at a low temperature gives the sulfenyl chloride,  $\text{Me}_2\text{ClCSCl}$ .<sup>200</sup>

Trithioacetone has been claimed as an aid to flotation,<sup>177</sup> and as an oil additive.<sup>415a</sup>

Trimeric thioketones have been prepared from methyl ethyl ketone,<sup>112</sup> cyclopentanone, cyclohexanone,<sup>246b</sup> indanone-1, 3-methylindanone-1, tetralone-1, and 3-methyl tetralone-1.<sup>140</sup> The trithioketones from methyl ethyl and diethyl ketones and from cyclohexanone have been claimed as constituents of an ointment.<sup>412</sup>

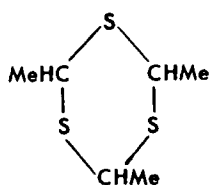
## Trithioacetophenone

This is the only one of the alkyl-aryl thiones that has received much attention. When hydrogen sulfide and hydrogen chloride are passed into a cold alcoholic solution of acetophenone, the blue monomeric thioacetophenone is formed. This soon changes to the colorless trimer, melting at  $122^\circ$ . This is believed to be the  $\beta$ -isomer. There should be an  $\alpha$  isomer but it has not been isolated.<sup>58c, 199</sup> Low temperature chlorination gives the sulfenyl chloride,  $\text{PhMeClCSCl}$ .<sup>200</sup>

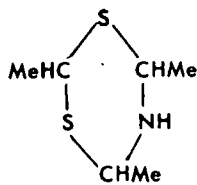


### Thialdines

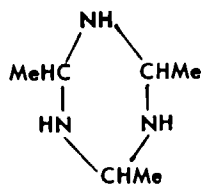
Thialdine is intermediate between trithioacetaldehyde and trimethyltrimethylene-triamine:



Trithioacetaldehyde



Thialdine



Trimethyl-trimethylene-triamine

Early investigators worked with acetaldehyde and gave the class name to the compound derived from it. The simpler compound, without the methyl groups, has to take the longer name thioformaldin to show that it is from formaldehyde.

### Thioformaldin

Thioformaldin is obtained, along with trithioformaldehyde and other products by treating formalin with hydrogen sulfide and ammonia. It is purified by long extraction with carbon disulfide. It cannot be purified by recrystallization since it is only slightly soluble in solvents and is decomposed by heating to 70°. It melts somewhere between 150° and 200°. On account of the lack of any way to assure its purity or to characterize it, its identity is doubtful. Analyses of different preparations show considerable variations. However, all the evidence points to the existence of a compound of the structure proposed even if it has never been obtained entirely free from impurities.<sup>405, 411, 439</sup>

The product from formaldehyde, hydrogen sulfide, and methylamine is N-methylthioformaldin.<sup>404, 707</sup> The same product is obtained from trimethyltrimethylene-triamine and hydrogen sulfide.<sup>186a, 186c, 186d, 280</sup>

Thioformaldin, or a product obtained by adding sulfur to it, is claimed as an addition agent for rubber.<sup>661</sup> The N-methyl derivative has been proposed as a pest control agent.<sup>612</sup>

Cyclohexylamine, formaldehyde, and hydrogen sulfide give 3-cyclohexyl-1,3-thiazetidine,  $C_6H_{11}N(CH_2)_2S$ , m. 120°, or 5-cyclohexyl-5,6-dihydro-,1,3,5-dithiazine,  $C_6H_{11}N(CH_2S)_2CH_2$ , m. 58°. <sup>104</sup>

## Thialdine

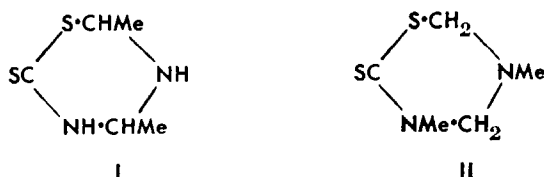
When hydrogen sulfide is passed into an aqueous solution of acetaldehyde and ammonia, thialdine, m.  $43^{\circ}$ ,  $d_{18}$  1.191<sup>705</sup> is obtained. It vaporizes at room temperature leaving no residue.<sup>59d, 124, 286a, 286b, 286c, 446a, 689, 705</sup> The crystal form<sup>549</sup> and heat of combustion<sup>187a</sup> of thialdine have been determined. The N-methyl<sup>233, 404, 446b</sup> and N-ethyl<sup>233, 404</sup> derivatives are obtained when these amines are substituted for the ammonia. Thialdine forms salts with acids<sup>59d, 124, 446a, 705</sup> and gives precipitates with silver, mercury,<sup>286c, 705</sup> copper,<sup>286c</sup> lead,<sup>286c, 705</sup> and ferric ions.<sup>286c</sup> N-Ethylthialdine gives precipitates with platinum salts.<sup>233</sup> Thialdine combines with methyl and ethyl iodides. The products appear to be quaternary ammonium iodides.<sup>327a</sup> It is oxidised to a disulfonic acid,  $\text{CH}_3\text{CH}(\text{SO}_3\text{H})_2$ , by permanganate.<sup>286a, 286b, 286c, 286d, 581b</sup> It is decomposed by sulfuric acid into ammonia and  $\alpha$ -trithioacetaldehyde.<sup>214</sup> By heating with silver oxide it was supposed to be converted to leucine,<sup>275</sup> but this has been disproved.<sup>327a</sup> Thialdine has been used in fermentation experiments as a soluble form of trithioacetaldehyde.<sup>507</sup>

Homologs of thialdine have been prepared from *i*-valeraldehyde,<sup>64, 526, 581a, 608</sup> heptaldehyde, and acrolein.<sup>581a</sup> Oil of rue which is methyl nonyl ketone, ammonia, and hydrogen sulfide give a crystalline compound supposed to belong to this class.<sup>688</sup> Thialdine-like compounds were obtained from ammonium sulfide and acetone.<sup>581a, 730</sup>

A seleno-thialdine has been prepared.<sup>705</sup>

## Carbothialdine

Aldehyde ammonia and carbon disulfide, in alcohol solution, give carbothialdine (I).<sup>556</sup> Acetaldehyde with ammonium dithiocarbamate,  $\text{NH}_2\text{CS}\cdot\text{SNH}_4$ , or with thiourea gives the same compound, having the composition  $\text{C}_5\text{H}_{10}\text{N}_2\text{S}_2$ .<sup>286c, 501</sup> An isomer of this (II) results from the reaction of carbon disulfide with trimethyltrimethylene-triamine.<sup>186a, 186c, 186d</sup> The same compound has been made from methylammonium methyldithiocarbamate.<sup>87</sup> There has been much discussion as to the structures of these, but they seem to be cleared up by a recent investigation.<sup>3</sup> The formulae assigned I is 2-thio-4,6-dimethyl-tetrahydro-1,3,5-thiadiazine and II is the 3,5-dimethyl-:

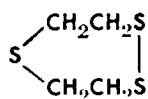


Carbothialdine in aqueous solution gives precipitates with silver<sup>286c, 556</sup> and lead ions.<sup>286c</sup> It is decomposed by heating with water<sup>161a, 556</sup> and is oxidised in hydrochloric acid solution to carbamine disulfide,  $(\text{NH}_2\text{CSS})_2$ .<sup>286a, 286c</sup>

*i*-Butyraldehyde,<sup>534</sup> *i*-valeraldehyde,<sup>286e, 501, 608</sup> and benzaldehyde<sup>501</sup> have been converted into carbothialdines by ammonia and carbon disulfide. The 3-phenyl-5-methyl- and several other analogs of II have been prepared.<sup>3</sup>

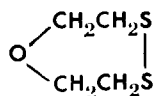
A compound which seems to belong to this class was obtained from triacetonediamine but was not well characterized.<sup>820</sup>

#### FOUR CARBON AND THREE SULFUR ATOMS



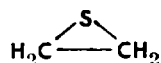
This compound, 1,2,5-trithiacycloheptane, is one of the products obtained from ethylene and sulfur at elevated temperatures.<sup>697</sup> It is formed by the oxidation of the sulfide-mercaptan. Its chemistry has not been developed. A compound of the same composition, but evidently a polymer, was prepared from mustard gas and alcoholic sodium sulfide.<sup>250</sup>

The analogous ether-disulfide,



has been isolated recently by the depolymerization of the polymeric disulfide,  $(\cdot\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}\cdot)_n$ . This was accomplished by the slow steam-distillation of the finely divided polymer.<sup>183, 184</sup> The properties of the monomer are  $b_D$  55–6°;  $d_{20/4}$  1.2737;  $n_{20/D}$  1.5823; molecular weight 137, calc. 136.<sup>184</sup> It polymerizes readily and copolymerizes with vinyl acetate<sup>650</sup> and with styrene.<sup>668</sup> A corresponding aromatic compound is obtained by steam distilling the tarry product formed when *ortho*-aminodiphenyldisulfide is diazotized.<sup>288.5</sup>

## Physical Properties of Some Cyclic Sulfides

ETHYLENE *epi*-SULFIDE AND DERIVATIVES

Ethylene sulfide, b. 53.5–50°; <sup>110</sup> 55–6°, <sup>186b</sup>, <sup>187c</sup>, <sup>189</sup>, <sup>327b</sup> 54–7°, <sup>356</sup> 55°, <sup>713</sup> 56°, <sup>510c</sup> 55.7°; <sup>402</sup> d 0/4 1.035, <sup>189</sup> 1.0368, <sup>187c</sup> d 15/4 1.0171, <sup>186b</sup> d 20/4 1.0046; <sup>287</sup> n 18/D 1.491, <sup>189</sup> 1.4914, <sup>187c</sup> n 19/D 1.49001, <sup>186b</sup> n 20/D 1.4914.<sup>287</sup>

2-Methyl-, b. 76°, <sup>713</sup> 75–7°, <sup>189</sup> 75–6°, <sup>174</sup> 72–5°, <sup>97</sup> 73–4°; <sup>451.5</sup> d 0/4 0.964, d 18/4 0.946; n 19/D 1.473, <sup>189</sup> n 15/D 1.4780.<sup>174</sup>

2-Ethyl-, b. 104, <sup>713</sup> 104–5°; d 0/4 0.944, d 18/4 0.930; n 19/D 1.475.<sup>189</sup>

2,2-Dimethyl-, b. 87°, <sup>174</sup> 84–6°; <sup>631a</sup> n 17/D 1.4661, <sup>174</sup> n 20/D 1.4641.<sup>631a</sup>

Trimethyl-, b. 145–50°; d 0/4 0.927.<sup>135</sup>

Tetramethyl-, m. 76.6°; b. 127°. <sup>713</sup>

Phenyl-, b<sub>0.01</sub> 25–8°; d 25/4 1.1044; n 20/D 1.6015.<sup>292</sup>

Tetraphenyl-, m. 179°. <sup>595a</sup>

Tetra-*p*-tolyl-, m. 195°. <sup>595a</sup>

Tetra-*p*-methoxyphenyl-, m. 210°, <sup>595a</sup>, <sup>601</sup> 205°. <sup>600</sup>

2-Vinyl-, b. 103–4°. <sup>173</sup>

2-Chloromethyl-, b<sub>760</sub> 138–9°, <sup>174</sup> b<sub>8</sub> 94–6°, <sup>347b</sup> b<sub>114</sub> 79–81°; n 20/D 1.5780.<sup>174</sup>

2-Mercaptomethyl-, b<sub>10</sub> 54–6°, <sup>623</sup> b<sub>30</sub> 77°; <sup>399</sup>, <sup>623</sup> d 20/4 1.1741.<sup>623</sup>

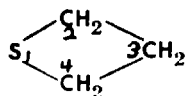
Cyclopentene sulfide, b<sub>65</sub> 69–70°; n 25/D 1.5222.<sup>675a</sup>

Cyclohexene sulfide, b. 180°, <sup>356</sup> b<sub>15</sub> 56–7°, <sup>618</sup> b<sub>16</sub> 67–8°, <sup>174</sup> b<sub>12</sub> 60–1.5°, b<sub>21</sub> 71.5–3.5°, <sup>675a</sup> b<sub>46</sub> 83–7°, <sup>631a</sup> b<sub>35</sub> 77–9°; <sup>97</sup> d 25/4 0.9274, <sup>356</sup> d<sub>25</sub> 1.068; <sup>494</sup> n 20/D 1.5309, <sup>174</sup> 1.5292, <sup>631a</sup> n 25/D 1.5311, <sup>675a</sup> 1.5317, <sup>494</sup> 1.4881.<sup>356</sup>

3-Methylcyclohexene sulfide, b<sub>25</sub> 85–6°; n 23/D 1.5097.<sup>173</sup>

Cyclohexylidene methylene episulfide, d<sub>25</sub> 1.065; n 25/D 1.5310.<sup>494</sup>

## TRIMETHYLENE SULFIDE AND DERIVATIVES



Trimethylene sulfide, CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>S, m. –73.25°; <sup>295.7</sup>, <sup>610</sup> b. 94.97°, <sup>610</sup> 95°, <sup>295.7</sup> 94°, <sup>189</sup>, <sup>713</sup> 93–5°, <sup>189</sup> b<sub>752</sub> 93.8–4.2°; <sup>282a</sup> d 0/4

1.051,<sup>189</sup> d 20/4 1.0200,<sup>295.7</sup> d 23/4 1.0284,<sup>282a</sup> d 25/4 1.01472, d 30/4 1.00957;<sup>295.7</sup> n 23/D 1.506,<sup>189</sup> 1.5059;<sup>282a</sup> surface tension 36.3 at 20°, 35.6 at 25°, 35.0 at 30°; viscosity 0.638 at 20°, 0.607 at 25°, 0.576 at 30°;<sup>295.7</sup> heat of vaporization at 0° 8560 cal./mole; heat of fusion 1971.4 cal./mole; other thermodynamic properties;<sup>610</sup> sulfone, m. 76°.<sup>282a</sup>

2-Methyl-, b. 106°,<sup>189</sup> b<sub>747</sub> 105.5–7.5°,<sup>282a</sup> 107°;<sup>713</sup> d 0/4 0.977,<sup>189</sup> d 20/4 0.9571;<sup>282a</sup> n 20/d 1.4830,<sup>189</sup> 1.4831; sulfone, b. 251–3.5°; d 16.5/4 1.2174; n 16.5/D 1.4700.<sup>282a</sup>

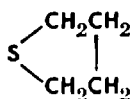
2,4-Dimethyl-, b<sub>757</sub> 112.5–3.5°; d 18/4 0.8710; n 18/D 1.4502; sulfone, b. 255–255.5°; d 17.6/4 1.1589; n 17.5/D 1.4653.<sup>282a</sup>

3,3-Dimethyl-, b. 120°; n 18/D 1.4739, n 35/D 1.4640; HgCl<sub>2</sub> m. 118°; sulfone, m. 55°; HgCl<sub>2</sub> m. 127°.<sup>30b</sup>

3-Hydroxy-, b<sub>1.3</sub> 57°; d 20/4 1.2130; n 20/D 1.5433.<sup>624a</sup>

3,3-Dihydroxymethyl-, m. 74°.<sup>84</sup>

#### TETRAMETHYLENE SULFIDE (THIOLANE, THIOPHANE) AND DERIVATIVES



Thiophane, m. -96.17°,<sup>339</sup> -96.16°,<sup>295.7</sup> -96.06°; b. 121.2°,<sup>699</sup> 120.9°,<sup>295.7</sup> 120.8°,<sup>195</sup> 120°;<sup>7</sup> 119–20°,<sup>659</sup> 119°,<sup>101c,</sup> 108, 713 118–9°,<sup>282b</sup> 118°,<sup>189</sup> 116–22°;<sup>728</sup> d 20/4 0.99869,<sup>295.7</sup> 0.9998, d 25/4 0.9947,<sup>699</sup> 0.99379,<sup>295.7</sup> d 18/4 0.9607;<sup>282b</sup> n 18/D 1.487,<sup>189</sup> 1.4871,<sup>282b</sup> n 21/D 1.5037,<sup>659</sup> n 20/D 1.5047, n 25/D 1.5022; HgCl<sub>2</sub> m. 128°,<sup>699</sup> 125.5°,<sup>282b</sup> 125°;<sup>728</sup> surface tension 35.8 at 20°, 35.0 at 25°, 34.6 at 30°; viscosity 1.042 at 20°, 0.971 at 25°, 0.914 at 30°;<sup>295.7</sup> heat of fusion 1757 cal./mole, other thermodynamic properties;<sup>339</sup> sulfoxide, b<sub>12</sub> 105–7°; n 25/D 1.5198;<sup>659</sup> sulfone, m. 28.36°,<sup>699</sup> 29°,<sup>346b</sup> 25°,<sup>490b</sup> 21°,<sup>27</sup> 20°,<sup>731</sup> 10°;<sup>282b</sup> b<sub>5</sub> 118°,<sup>490b</sup> b<sub>11</sub> 141–2°,<sup>346b</sup> b<sub>15</sub> 149.5–50°,<sup>27</sup> b<sub>18</sub> 153–4°,<sup>282b,</sup> 731 b<sub>743</sub> 285–8°;<sup>282b</sup> d 18.2/4 1.2723; n 18.2/D 1.4833.<sup>282b</sup>

2-Carboxy-, m. 53°; amide, m. 132°.<sup>546</sup>

2,3-Dicarboxy-, dihydrazide, m. 209°.<sup>120</sup>

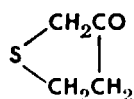
2,5-Dicarboxy-, m. 136°;<sup>672</sup> DL *trans*, m. 166°; D and L, m. 180°; meso (*cis*), m. 145°;<sup>238c</sup> diEt ester, b<sub>0.5</sub> 100°; n. 26/D 1.4808; diamide, m. 181°;<sup>672</sup> imide, m. 156°; monoanilide, m. 140°; N-benzylimide, m. 114°;<sup>333.5</sup> anhydride, m. 142°,<sup>672</sup> *cis*, m. 150°.<sup>333.5</sup>

- 3,4-Dicarboxy-, *trans*, m. 125°; *cis*, m. 158°;<sup>38</sup> anhydride, m. 135°.<sup>119</sup>
- 2- $\delta$ -Carboxybutyl-3,4-dicarboxy-, m. 105–10°.<sup>38</sup>
- 3,3,4,4-Tetracarbethoxy-,  $b_8$  192–200°.<sup>371</sup>
- 3,4-Dihydroxy-, m. 54–8°.<sup>371</sup>
- 3,4-Diethoxy-, m. 53°.<sup>528</sup>
- 2-Hydroxy-3-bromo-, sulfone, m. 191°; Ac., m. 120°.<sup>32</sup>
- 2-(4-carbomethoxybutyl)-,  $HgCl_2$ , m. 86°.<sup>497</sup>
- 2-Aminomethyl-,  $b_{10}$  69.5°;  $d$  15/4 1.0920;  $n$  15/D 1.5399.<sup>546</sup>
- 2,3-(—NHCO<sub>2</sub>Et)<sub>2</sub>, m. 152–4°.<sup>120</sup>
- 3,4-Diamino-, 1st form, m. 40°; diAc., m. 260–5°; diBz., m. 295–300°.<sup>371</sup> 2nd form, diAc., m. 175°; diBz., m. 239°.<sup>372</sup> 3rd form, diAc., m. 208°; diBz., m. 269°.<sup>372</sup>
- 3,4-Dichloro-, m. 61°.<sup>371</sup>
- 2,3,4,5-Tetrachloro-,  $\alpha$ -isomer, m. 113.5;<sup>129b</sup>, <sup>167</sup>  $b_{3-4}$  111.5°;<sup>129b</sup>  $\beta$ -isomer, m. 46°;<sup>167</sup>, <sup>168</sup>  $b_5$  110–8°;  $n$  50/D 1.5688.<sup>168</sup>
- 2,2,3,4,5-Pentachloro-, m. 32°;  $n$  35/D 1.5755.<sup>167</sup>
- 2,2,3,4,5,5-Hexachloro-, m. 46°;  $b_1$  100–5°;  $n$  50/D 1.5590.<sup>167</sup>
- Octachloro-, m. 222.5°.<sup>168</sup>
- 3,4-Dibromo-,  $b_3$  83–9°;<sup>371</sup> sulfone, m. 141°.<sup>32</sup>
- 3-Mercapto-,  $b_{30}$  95°;  $n$  20/D 1.5780.<sup>468</sup>
- 3,4-Dimercapto-, sulfone, m. 128°; Ac., m. 156°.<sup>529</sup>
- 2-Ethylmercapto-,  $b_2$  83°;  $n$  20/D 1.5485.<sup>82b</sup>
- 2-Propylmercapto-,  $b_{2.5}$  95°;  $n$  20/D 1.5350.<sup>82b</sup>
- 2-*t*-Butylmercapto-,  $b_2$  90°;  $n$  20/D 1.5350.<sup>82b</sup>
- 2-Phenylmercapto-,  $b_1$  130–5°.<sup>82b</sup>
- 2-Benzylmercapto-,  $b_{2.5}$  162°;  $n$  20/D 1.61.<sup>82b</sup>
- 2-Cyclohexylmercapto-,  $b_3$  144–8°;  $n$  20/D 1.5580.<sup>82b</sup>
- 3-Ethylmercapto-,  $b_2$  76–81°;  $n$  20/D 1.5500.<sup>82b</sup>
- 3-Propylmercapto-,  $b_2$  85–90°;  $n$  20/D 1.5410.<sup>82b</sup>
- 3-Phenylmercapto-,  $b_{2.5}$  140–5°;  $n$  20/D 1.6250.<sup>82b</sup>
- 3-Benzylmercapto-,  $b_3$  160–5°;  $n$  20/D 1.605.<sup>82b</sup>
- 3,3-Diethylmercapto-,  $b_{2.5}$  112–4°;<sup>52</sup>  $b_{12}$  154°;<sup>363</sup>  $n$  25/D 1.5669;<sup>52</sup> disulfone, m. 197°;<sup>363</sup> trisulfone, m. 193.5°.<sup>52</sup>
- 2-Keto-, (thiobutyrolactone),  $b_3$  55–6°;<sup>830</sup>  $b_{20}$  90–2°;<sup>37</sup>  $b_{52}$  110.5°;  $d$  20/4 1.1635,<sup>728</sup> 1.1778;  $n$  20/D 1.5242,<sup>330</sup> 1.5189.<sup>728</sup>
- 2,5-Diketo-, m. 31°.<sup>15a</sup>, <sup>694</sup>
- 3,4-Dithiono-,  $b_2$  120–5°;<sup>129a</sup> 121–3°;  $d$  25/4 1.441.<sup>115</sup>
- 2-Methyl-, m. –100.71°;  $b$ . 132.4°;<sup>699</sup> 133°;<sup>7</sup> 134°;<sup>106b</sup>  $b_{750}$  132°;<sup>408</sup> 132.5–2.6°;<sup>282b</sup>  $d$  20/4 0.960,<sup>408</sup> 0.9552,  $d$  25/4 0.9512,<sup>699</sup>  $d$  18/4

- 0.9564; n 15/D 1.4886,<sup>282b</sup> n 20/D 1.4920,<sup>408</sup> 1.4909, n 25/D 1.4884;<sup>699</sup> 2 HgCl<sub>2</sub>, m. 162°; <sup>699</sup> sulfone, m. -22°; <sup>699</sup> b<sub>758</sub> 279-80°; d 14/4 1.207; n 14/D 1.4801,<sup>282b</sup> n 20/D 1.4810.<sup>699</sup>
- 3-Methyl-, m. -81.16°; b. 138.2°;<sup>699</sup> 138°;<sup>7</sup> b<sub>740</sub> 137.5-8.5°; d 18.5/4 0.9596,<sup>282b</sup> d 20/4 0.9634, d 25/4 0.9585; n 20/4 1.4924, n 25/D 1.4902,<sup>699</sup> n 18.5/D 1.4886; HgCl<sub>2</sub>, m. 83°;<sup>282b</sup> 109.5°; <sup>699</sup> sulfone, m. 1°;<sup>27</sup> 0.5°; n 20/D 1.4770.<sup>699</sup>
- 2-Methyl-5-keto-, (γ-thiovalerolactone) b. 214-6°, b<sub>8</sub> 85-6°; d 20/4 1.0975; n 20/D 1.5028.<sup>583</sup>
- 2-Methyl-3-hydroxy-3-carbamyl-4-carbethoxy, m. 157°.<sup>590</sup>
- 3-Methyl-3-bromo-, b<sub>11</sub> 75°.<sup>363</sup>
- 3-Methyl-3-hydroxy-, m. 46°; b<sub>10</sub> 65-70°.<sup>363</sup>
- 3-Methyl-3,4-dichloro-, b<sub>3</sub> 68-70°; HgCl<sub>2</sub>, m. 158°; sulfone, m. 145.5°.<sup>33b</sup>
- 3-Methyl-heptachloro-, m. 218.5°.<sup>642</sup>
- 3-Methyl-2,3,4,5-tetrachloro-2-carbomethoxy-, m. 53.5°.<sup>642.5</sup>
- 2,2-Dimethyl-5-keto-4-carboxy-, m. 91°.<sup>629</sup>
- 2,4-Dimethyl-, b<sub>742</sub> 197-8°; d 20/4 0.9265; n 20/D 1.4818; HgCl<sub>2</sub>, m. 89°;<sup>717</sup> sulfone, b<sub>5</sub> 123.3°; d 20/4 1.1362; n 25/D 1.4733.<sup>486</sup>
- 2,5-Dimethyl-, b<sub>756</sub> 142-2.2°;<sup>282b</sup> 142°;<sup>713</sup> 141°;<sup>727</sup> d 0/4 0.9391,<sup>282b</sup> d 20/4 0.9220,<sup>727</sup> d 21.5/4 0.9175, d 100/4 0.8415;<sup>282b</sup> n 20/D 1.4822,<sup>727</sup> n 21.5/D 1.4752;<sup>282b</sup> sulfone, b<sub>749</sub> 277.5-8°; d 18/4 1.1532; n 18/D 1.4772;<sup>282b</sup> *cis*-, m. -89.4°; b<sub>45</sub> 60.0°; d 20/4 0.9222, d 25/4 0.9177; n 20/D 1.4799, n 25/D 1.4774; 2 HgCl<sub>2</sub> m. 180°; sulfone, m. -4.0°; n 20/D 1.4761;<sup>699</sup> *trans*-, m. -76.35°; b<sub>44</sub> 58.0°; d 20/4 0.9188, d 25/4 0.9142; n 20/D 1.4776, n 25/D 1.4752; HgCl<sub>2</sub>, m. 111°;<sup>699</sup> 110°;<sup>282b</sup> sulfone, m. 3°; n 20/D 1.4760.<sup>699</sup>
- 3,4-Dimethyl-, sulfone, m. 51°; b. 260-5°, b<sub>15</sub> 136-7°.<sup>27</sup>
- 3,4-Dimethyl-3,4-dichloro-, m. 174°; sulfone, m. 265°.<sup>33b</sup>
- 2,3,4,5-Tetramethyl-, sulfone, b<sub>2</sub> 117°, b<sub>14</sub> 152-4°.<sup>27</sup>
- 2-Ethyl-, b. 136-9°;<sup>139</sup> b<sub>742</sub> 155.5-6.5°; d 20/4 0.9451; n 20/D 1.4896,<sup>716</sup> 1.4871; HgCl<sub>2</sub>, m. 100°, 2 HgCl<sub>2</sub>, m. 210°.<sup>139</sup>
- 2-Ethyl-5-Methyl-, 2 HgCl<sub>2</sub>, m. 146-8°.<sup>139</sup>
- 3-Ethynyl-3-hydroxy-, m. 45°.<sup>363</sup>
- 2-Propyl-3,4-dicarboxy-, *trans*, m. 157°.<sup>38</sup>
- 2,5-Dipropyl-, b<sub>1</sub> 74-5°; d 20/4 0.8958; n 20/D 1.4795; sulfone, b<sub>1</sub> 123-5°; d 20/4 1.048; n 20/D 1.4719.<sup>452</sup>
- 3,4-Dipropyl-, b<sub>1</sub> 65-6°; d 20/4 0.9111; n 20/D 1.4830; sulfone, m. 59.5°.<sup>452</sup>

- 2-( $\gamma$ -Phenoxypropyl)-3-benzamido-4-carbethoxy-, m.  $99^\circ$ .<sup>156</sup>  
 2-( $\gamma$ -Phenoxypropyl)-3,4-dicarboxy-, *trans*, m.  $183^\circ$ .<sup>88</sup>  
 2-( $\gamma$ -Benzyloxypropyl)-3-benzamido-4-carbethoxy-, m.  $66^\circ$ .<sup>156</sup>  
 2-Butyl-,  $\text{HgCl}_2$ , m.  $101^\circ$ .<sup>139</sup>  
 2-*t*-Butyl-, b.  $186-7^\circ$ ; n 20/D  $1.4850$ .<sup>315</sup>  
 3-Hydroxy-3-carboxydiphenylmethyl-, m.  $91^\circ$ .<sup>85</sup>  
 3-Phenyl-3-hydroxy-,  $b_{0.025}$   $85-90^\circ$ .<sup>363</sup>  
 2-Phenyl-3-carbethoxy-4-cyano-4-hydroxy-, m.  $124.5^\circ$ .<sup>654</sup>  
 2-Benzyl-, m.  $51^\circ$ ;  $\text{HgCl}_2$  m.  $175^\circ$ .<sup>139</sup>

## THIOPHANONE-3 AND DERIVATIVES

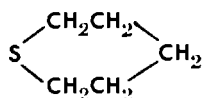


- 3-Thiophanone,  $b_7$   $58.2-8.4^\circ$ ,<sup>712</sup>  $b_{15}$   $74.5^\circ$ ,<sup>664</sup>  $b_{24}$   $84-5^\circ$ ,<sup>364</sup>  $b_{29}$   $83.5^\circ$ ,<sup>125</sup> b.  $175^\circ$ ,<sup>326</sup> oxime, m.  $36^\circ$ ,<sup>363</sup> semicarbazone, m.  $192^\circ$ ,<sup>326, 359, 364</sup>  $196^\circ$ .<sup>125</sup>  
 2-Methyl-,  $b_{11}$   $90-100^\circ$ ,<sup>364</sup>  $b_{13}$   $67^\circ$ ,<sup>575</sup>  $b_{28}$   $82^\circ$ ,<sup>125</sup> semicarbazone, m.  $193.5^\circ$ ,<sup>364</sup>  $186^\circ$ .<sup>125</sup>  
 2-Tetradecyl-, m.  $45.5^\circ$ ;  $b_{0.03}$   $138-45^\circ$ ; semicarbazone, m.  $158^\circ$ .<sup>585</sup>  
 2- $\delta$ -Methoxybutyl-,  $b_{0.05}$   $102-3^\circ$ .<sup>364</sup>  
 2- $\gamma$ -Phenoxypropyl-, m.  $43^\circ$ .<sup>155</sup>  
 2- $\delta$ -Methoxybutyl-4-carbethoxy,  $b_{0.001}$   $115^\circ$ .<sup>364</sup>  
 2-Methyl-4-carbethoxy-,  $b_{11}$   $123-30^\circ$ ,<sup>364</sup>  $b_{4.5}$   $93-5^\circ$ ,<sup>125</sup>  $b_{13}$   $124^\circ$ .<sup>575</sup>  
 4-Methyl-,  $b_{11}$   $80-90^\circ$ ,<sup>364</sup>  $b_{18}$   $77-8^\circ$ ; semicarbazone, m.  $199^\circ$ .<sup>395c</sup>  
 4-Methyl-2-carbethoxy-,  $b_{18}$   $128-31^\circ$ .<sup>395c</sup>  
 4-Ethyl-,  $b_{21}$   $85^\circ$ .<sup>268</sup>  
 4-Ethyl-2-carbethoxy-,  $b_{15.5}$   $132-4^\circ$ .<sup>268</sup>  
 5-Methyl-,  $b_{12}$   $60-70^\circ$ ,<sup>23</sup>  $b_{17}$   $77^\circ$ ,<sup>396</sup> semicarbazone, m.  $185^\circ$ ,<sup>396</sup>  $174^\circ$ .<sup>23</sup>  
 5-Methyl-2-carbethoxy-,  $b_{17}$   $134-7^\circ$ .<sup>396</sup>  
 5-Ethyl-,  $b_{12}$   $72-3^\circ$ .<sup>23</sup>  
 5-Phenyl-, m.  $55^\circ$ ; semicarbazone, m.  $206^\circ$ .<sup>654</sup>  
 5-Phenyl-4-carbethoxy-, m.  $77^\circ$ .<sup>654</sup>  
 2-Carbomethoxy-,  $b_9$   $116-6.5^\circ$ ; semicarbazone, m.  $187.5^\circ$ .<sup>712</sup>  
 2-Carbethoxy-,  $b_2$   $104-110^\circ$ ,<sup>480</sup>  $b_{11}$   $123-6^\circ$ .<sup>326</sup>  
 4-Carbomethoxy-, m.  $38^\circ$ ;  $b_{20}$   $128.5-9.5^\circ$ ,<sup>712</sup>  $128.5^\circ$ ,<sup>664</sup> semicarbazone, m.  $190^\circ$ .<sup>712</sup>  
 4-Carbethoxy-,  $b_1$   $90-3^\circ$ ,<sup>119</sup>  $b_4$   $96^\circ$ ,<sup>125</sup>  $b_{11}$   $124-9^\circ$ ,<sup>364</sup> phenylhydrazones, m.  $101^\circ$ ,<sup>125</sup> semicarbazone, m.  $173^\circ$ .<sup>119</sup>



- 2- $\beta$ -Carbethoxyethyl-, m.  $51^\circ$ ;  $b_{0.03}$   $132-5^\circ$ .<sup>361</sup>  
 2- $\beta$ -Carbethoxyethyl-2-carbethoxy-,  $b_{15}$   $195-8^\circ$ .<sup>23</sup>  
 2- $\beta$ -Carbethoxyethyl-4-carbethoxy-,  $b_{0.04}$   $130-3^\circ$ .<sup>361</sup>  
 2- $\beta$ -Carbethoxyethyl-4-hydroxy-, m.  $130^\circ$ .<sup>361</sup>  
 2-( $\delta,\delta$ -Dicarbethoxybutyl)-2-carbethoxy-,  $b_{0.2}$   $170-80^\circ$ .<sup>23</sup>  
 2- $\iota$ -Carboxynonyl-, m.  $70-1^\circ$ ;  $b_{0.03}$   $178-85^\circ$ .<sup>585</sup>  
 4-Carboxy-2- $\delta$ -carboxybutyl, di Et ester, m.  $119^\circ$ ; <sup>156</sup>  $b_{13}$   $140-1^\circ$ .<sup>575</sup>

## PENTAMETHYLENE SULFIDE AND DERIVATIVES



- Pentamethylene sulfide,  $\text{CH}_2(\text{CH}_2\text{CH}_2)_2\text{S}$ , m.  $19.07^\circ$ ,<sup>699</sup>  $16^\circ$ ,<sup>408</sup>  $13^\circ$ ; <sup>159</sup> b.  $141.6^\circ$ ,<sup>699</sup>  $142^\circ$ ,<sup>7</sup>  $141^\circ$ ,<sup>101c</sup>  $106b$ , <sup>108</sup>  $140^\circ$ ,<sup>618</sup>  $140-2^\circ$ ; <sup>106a</sup>  $b_{756}$   $140^\circ$ ,<sup>504a</sup>  $b_{755}$   $141^\circ$ ,<sup>159</sup>  $b_{750}$   $141^\circ$ ,<sup>408</sup>  $b_{747}$   $141.5-2^\circ$ ,<sup>282c</sup>  $139.4-40^\circ$ ; <sup>723</sup> d  $15/4$   $0.9889$ ,<sup>159</sup> d  $18/4$   $0.9943$ ,<sup>282c</sup> d  $20/4$   $0.9849$ ,<sup>159</sup>  $0.9791$ ,<sup>723</sup>  $0.9856$ , d  $25/4$   $0.9810$ ; <sup>699</sup> n  $18/D$   $1.5046$ ,<sup>282c</sup> n  $20/D$   $1.5048$ ,<sup>723</sup>  $1.5067$ ,<sup>699</sup>  $1.5055$ ,<sup>504a</sup>  $1.5057$ ,<sup>408</sup> n  $25/D$   $1.5041$ ; <sup>699</sup>  $\text{HgCl}_2$  m.  $139^\circ$ ,<sup>699</sup>  $137.5^\circ$ ,<sup>282c</sup>  $149^\circ$ ;  $\text{MeI}$   $138.5^\circ$ ; <sup>282d</sup> sulfone, m.  $97^\circ$ ,<sup>699</sup>  $94.5^\circ$ ,<sup>7</sup>  $99^\circ$ .<sup>282c</sup>
- 2-Methyl-, m.  $-58.14^\circ$ ;  $b_{26}$   $55.0^\circ$ ,<sup>699</sup> b.  $151^\circ$ ,<sup>713</sup>  $154-6^\circ$ ,<sup>101c</sup>  $b_{750}$   $151^\circ$ ,<sup>408</sup>  $151.4-1.6^\circ$ ; <sup>282c</sup> d  $0/4$   $0.9616$ , d  $18.5/4$   $0.9449$ ,<sup>282c</sup> d  $20/4$   $0.9428$ , d  $25/4$   $0.9381$ ; <sup>699</sup> n  $18.5/D$   $1.4884$ ,<sup>282c</sup> n  $20/D$   $1.4905$ ,<sup>699</sup>  $1.4898$ ,<sup>408</sup> n  $25/D$   $1.4881$ ; <sup>699</sup>  $\text{HgCl}_2$ , m.  $102^\circ$ ,<sup>699</sup>  $98^\circ$ ; <sup>282c</sup> sulfone, m.  $66^\circ$ ,<sup>699</sup>  $68.5^\circ$ ;  $b_{749}$   $295-6.5^\circ$ .<sup>282c</sup>
- 2,5-Dimethyl-4-ethyl-4-hydroxy-,  $b_8$   $110-1^\circ$ ; d  $20/4$   $1.0344$ ; n  $20/D$   $1.5140$ .<sup>505b</sup>
- 2,5-Dimethyl-4-ethynyl-4-hydroxy-,  $b_3$   $88^\circ$ ; d  $20/4$   $1.0680$ ; n  $20/D$   $1.5250$ .<sup>505b</sup>
- 3-Methyl-, m.  $-60.17^\circ$ ; b.  $157-9^\circ$ ; d  $20/4$   $0.9473$ , d  $25/4$   $0.9430$ ; n  $20/D$   $1.4922$ , n  $25/D$   $1.4899$ ;  $\text{HgCl}_2$ , m.  $136^\circ$ ; sulfone, m.  $83^\circ$ .<sup>699</sup>
- 4-Methyl-, m.  $-28.11^\circ$ ;  $b_{22}$   $54.0^\circ$ ; d  $20/4$   $0.9471$ , d  $25/4$   $0.9427$ ; n  $20/D$   $1.4923$ , n  $25/D$   $1.4899$ ;  $\text{HgCl}_2$ , m.  $136^\circ$ ; sulfone, m.  $121.5^\circ$ .<sup>699</sup>
- 2,3,6-Trimethyl-4-ethynyl-4-hydroxy-,  $b_5$   $102-2.5^\circ$ ; d  $0/4$   $1.0471$ ; n  $20/D$   $1.5185$ .<sup>505b</sup>
- 2,2,6,6-Tetramethyl-,  $b_9$   $93^\circ$ ,<sup>504b</sup>  $b_{11}$   $61^\circ$ ,<sup>14</sup>  $b_{12}$   $66^\circ$ ,<sup>504a</sup>, <sup>618</sup>  $b_{15}$   $66^\circ$ ; <sup>14</sup> n  $17/D$   $1.4858$ ,<sup>504b</sup> n  $19/D$   $1.4763$ .<sup>504a</sup>

- 2,2,6,6-Tetramethyl-4-hydroxy-, m.  $70^{\circ}$ .<sup>14</sup>  
 2,6,6-Trimethyl-2-ethyl-,  $b_{13}$   $87^{\circ}$ ; n 20/D 1.4849.<sup>504a</sup>  
 4-Hydroxymethyl-,  $b_{18}$   $138^{\circ}$ ; phenylurethane, m.  $130^{\circ}$ .<sup>541</sup>  
 4- $\beta$ -Hydroxyethyl-,  $b_{10}$   $145^{\circ}$ .<sup>542</sup>  
 4-Carboxy-, m.  $112.5^{\circ}$ ; Et ester,  $b_{15}$   $118-20^{\circ}$ ; amide, m.  $184.5^{\circ}$ .<sup>541</sup>  
 4-Carboxymethyl-, m.  $169-71^{\circ}$ ; Et ester  $b_{10}$   $137-43^{\circ}$ .<sup>542</sup>  
 4,4-Diethylmercapto-,  $b_2$   $112-4^{\circ}$ ; n 20/D 1.5635; 1-sulfone,  $b_2$   $172-5^{\circ}$ ; n 25/D 1.5505; trisulfone, m.  $171.5^{\circ}$ .<sup>52</sup>  
 2-Methyl-4,4-diethylmercapto-,  $b_2$   $112-4^{\circ}$ ; n 20/D 1.5552.<sup>52</sup>  
 3-Methyl-4,4-diethylmercapto-,  $b_2$   $114-6^{\circ}$ ; n 25/D 1.5625.<sup>52</sup>  
 2,6-Dimethyl-4,4-diethylmercapto-,  $b_{1.5}$   $108-10^{\circ}$ ; n 25/D 1.5418; trisulfone, m.  $200.5^{\circ}$ .<sup>52</sup>  
 2,6-Dimethyl-4,4-diethylmercapto-3-carbomethoxy-, m.  $52^{\circ}$ ;  $b_{2.5}$   $144-6^{\circ}$ ; trisulfone, m.  $170^{\circ}$ .<sup>52</sup>  
 2,6-Dicarboxy-, m.  $213^{\circ}$ ; diMe ester  $b_{25}$   $170-80^{\circ}$ ; anhydride, m.  $169^{\circ}$ ; <sup>228</sup> *cis*, m.  $208-10^{\circ}$ .<sup>607d</sup>  
 3-Bromo-,  $b_4$   $68-9^{\circ}$ .<sup>228</sup>  
 3-Hydroxy-,  $b_{24}$   $114-8^{\circ}$ .<sup>228</sup>  
 4-Hydroxy-4-cyano-, m.  $63^{\circ}$ .<sup>78</sup>  
 4-Hydroxy-4-carboxy-, m.  $133^{\circ}$ ; sulfone m.  $208^{\circ}$ .<sup>78</sup>  
 4-Phenyl-4-hydroxy-, m.  $78^{\circ}$ ; sulfone, m.  $197^{\circ}$ .<sup>78</sup>  
 4-Phenyl-4-cyano-, m.  $57^{\circ}$ ; <sup>207, 208</sup>  $b_5$   $175^{\circ}$ ; sulfone, m.  $149^{\circ}$ .<sup>208</sup>  
 4-Phenyl-4-carboxy-, m.  $158^{\circ}$ ; <sup>207, 208, 209</sup> sulfone, m.  $215^{\circ}$ ; <sup>207, 208</sup> amide, m.  $159^{\circ}$ .<sup>207, 208, 209</sup>  
 4-Benzyl-4-hydroxy-, m.  $51^{\circ}$ ; sulfone, m.  $152.5^{\circ}$ .<sup>78</sup>  
 2-Keto-, (thiovaleric lactone),  $b_{2.5}$   $79-80^{\circ}$ ,  $b_{12}$   $105-6^{\circ}$ ,<sup>583</sup>  $b_{25}$   $150-2^{\circ}$ ; <sup>37</sup> d 20/4 1.1550; n 20/D 1.5314.<sup>583</sup>  
 3-Keto-,  $b_{18}$   $101-2^{\circ}$ .<sup>226</sup>  
 3-Keto-2-carbethoxy-,  $b_4$   $117-20^{\circ}$ .<sup>226</sup>  
 4-Keto-, m.  $66^{\circ}$ ,<sup>53, 76</sup>  $62^{\circ}$ ; <sup>227a</sup> oxime, m.  $85^{\circ}$ ; semicarbazone, m.  $151^{\circ}$ ; <sup>76</sup> sulfoxide, m.  $113^{\circ}$ ; <sup>78</sup> sulfone, m.  $222^{\circ}$ , <sup>227a</sup>  $172^{\circ}$ , <sup>13</sup>  $170^{\circ}$ .<sup>78</sup>  
 4-Keto-2-methyl-,  $b_2$   $41-5^{\circ}$ ,<sup>53</sup>  $b_{12}$   $82.5^{\circ}$ ; <sup>505a</sup> d 20/4 1.0877; n 20/D 1.5094,<sup>505a</sup> n 25/D 1.5125; <sup>53</sup> semicarbazone, m.  $168^{\circ}$ .<sup>505a</sup>  
 4-Keto-3-methyl-,  $b_{1.5}$   $43-8^{\circ}$ ; n 25/D 1.5175.<sup>53</sup>  
 4-Keto-2,6-dimethyl-, m.  $38.5^{\circ}$ ; <sup>13, 14</sup>  $b_{2.5}$   $46-9^{\circ}$ ,<sup>53</sup>  $b_{18}$   $93-4^{\circ}$ ; <sup>14</sup> n 25/D 1.4906; <sup>53</sup> semicarbazone, m.  $196^{\circ}$ .<sup>14</sup>  
 4-Keto-2,6-dimethyl-3-carbomethoxy-, m.  $86^{\circ}$ ,<sup>13, 14</sup>  $83.5^{\circ}$ .<sup>53</sup>  
 4-Keto-2,6-dimethyl-3,5-dicarbethoxy-,  $b_{14}$   $88^{\circ}$ ; semicarbazone, m.  $183^{\circ}$ .<sup>334</sup>

4-Keto-2,2,6,6-tetramethyl-,  $b_4$   $74^\circ$ ,  $b_{16}$   $98^\circ$ ; semicarbazone, m.  $216^\circ$ .<sup>14</sup>

4-Keto-3-carboxy-, Me ester  $b_5$   $120^\circ$ ; n 20/D 1.5234; <sup>227a</sup> Et ester, m.  $59^\circ$ .<sup>76</sup>

### HIGHER CYCLIC SULFIDES

Hexamethylene sulfide,  $(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$ , b.  $170^\circ$ ,<sup>713</sup>  $b_{750}$   $174^\circ$ ,<sup>408</sup>  $b_{747}$   $169-71^\circ$ ; d 18/4 0.9743; n 18/D 1.5044,<sup>282d</sup> n 20/D 1.5125; <sup>408</sup> sulfone, m.  $71^\circ$ .<sup>282d</sup>

Dodecamethylene sulfide,  $(\text{CH}_2)_{12}\text{S}$ , m.  $66.5^\circ$ .<sup>498</sup>

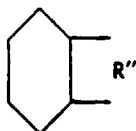
Tridecamethylene sulfide,  $(\text{CH}_2)_{13}\text{S}$ , m.  $66^\circ$ .<sup>498</sup>

Tetradecamethylene sulfide,  $(\text{CH}_2)_{14}\text{S}$ , m.  $72.5^\circ$ ,<sup>498</sup>  $71^\circ$ ;  $\text{HgCl}_2$  m.  $167^\circ$ .<sup>73</sup>

Hexadecamethylene sulfide,  $(\text{CH}_2)_{16}\text{S}$ , m.  $61^\circ$ ;  $\text{HgCl}_2$  m.  $166^\circ$ .<sup>73</sup>

Octadecamethylene sulfide,  $(\text{CH}_2)_{18}\text{S}$ , m.  $74^\circ$ ;  $b_{16}$   $186^\circ$ ;  $\text{HgCl}_2$  m.  $125^\circ$ .<sup>73</sup>

### BENZOCYCLIC SULFIDES



R''

— $\text{CH}_2\text{SCH}_2$ —, m.  $26^\circ$ ;  $b_{14}$   $108^\circ$ ; d 26/4 1.143.<sup>107</sup>

— $\text{CH}_2\text{CH}_2\text{S}$ —,  $b_{13}$   $104^\circ$ ; d 21/4 1.129.<sup>107</sup>

— $\text{CH}_2\text{CH}_2\text{CH}_2\text{S}$ —,  $b_{15}$   $128-30^\circ$ ; sulfone, m.  $88.5^\circ$ .<sup>106b</sup>

— $\text{COCH}_2\text{CH}_2\text{S}$ —, m.  $30^\circ$ ;  $b_{0.1}$   $113-4^\circ$ .<sup>370</sup>

— $\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2$ —, m.  $96^\circ$ ;  $b_{14}$   $141-5^\circ$ ; sulfone, m.  $176^\circ$ .<sup>107</sup>

— $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{S}$ —,  $b_{21}$   $140-1^\circ$ .<sup>131</sup>

### CYCLIC SELENIDES

Trimethylene,  $\text{CH}_2(\text{CH}_2)_2\text{Se}$ ,  $b_{779}$   $118-9^\circ$ ; d 20/4 1.5275; <sup>238a</sup>, <sup>482c</sup> n 16/D 1.5612;  $\text{I}_2$  m.  $98^\circ$ .<sup>238a</sup>

Tetramethylene,  $(\text{CH}_2\text{CH}_2)_2\text{Se}$ ,  $b_{770}$   $135-6^\circ$ ,  $b_{172}$   $90-1^\circ$ ; d 18/4 1.484; n 18/D 1.5510;  $\text{Cl}_2$  m.  $89^\circ$ ;  $\text{Br}_2$  m.  $92^\circ$ ;  $\text{I}_2$  m.  $100^\circ$ ;  $\text{HgCl}_2$  m.  $179^\circ$ ;  $\text{MeI}$  m.  $174^\circ$ .<sup>482a</sup>

— 2,5-dicarboxy-, *trans*, L, m.  $143^\circ$ .<sup>238b</sup>

— 2,3,4,5-tetrachloro-, m.  $97^\circ$ .<sup>652</sup>

— 2,2,5,5-tetrachloro-, m.  $98^\circ$ ; selenoxide, m.  $150^\circ$ .<sup>652</sup>

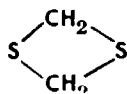
— 2,2,3,4,5,5-hexachloro-, m.  $55^\circ$ ; selenoxide, m.  $172.5^\circ$ .<sup>652</sup>

- 2,3,4,5-tetrachloro-2,5-dibromo-, m.  $72^{\circ}$ .<sup>652</sup>  
 — 2,2,5,5-tetrabromo-, m.  $97^{\circ}$ ; Br<sub>2</sub> m.  $152^{\circ}$ ; selenoxide, m.  $130^{\circ}$ .<sup>652</sup>  
 Pentamethylene, CH<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>Se, b.  $158^{\circ}$ ; d 20/4 1.399; n 18/D 1.5475; HgCl<sub>2</sub> m.  $176^{\circ}$ ; Cl<sub>2</sub> m.  $103^{\circ}$ ; Br<sub>2</sub> m.  $118^{\circ}$ ; I<sub>2</sub> m.  $114^{\circ}$ .<sup>482b</sup>  
 Hexamethylene, (•CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>Se, b<sub>756</sub>  $188-90^{\circ}$ , b<sub>68</sub>  $105^{\circ}$ ; d 24.5/4 1.353; n 18/D 1.5470; HgCl<sub>2</sub> m.  $194^{\circ}$ ; Cl<sub>2</sub> m.  $78^{\circ}$ ; Br<sub>2</sub> m.  $119^{\circ}$ ; I<sub>2</sub> m.  $82^{\circ}$ .<sup>482d</sup>  
 Selenothiane, S(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>Se, m.  $107^{\circ}$ ,<sup>269</sup>  $104^{\circ}$ .<sup>354</sup>  
 Selenoxane, Se(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, m.  $-21.5^{\circ}$ ; b<sub>548</sub>  $156.6^{\circ}$ , b<sub>37</sub>  $79.5^{\circ}$ ; n 20/D 1.5480.<sup>354</sup>

## CYCLIC TELLURIDES

- Tetramethylene, (•CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>Te, b.  $167^{\circ}$ ; n 18/D 1.6175; <sup>482e</sup> Cl<sub>2</sub> m.  $113^{\circ}$ ; Br<sub>2</sub> m.  $128-31^{\circ}$ ; <sup>224</sup> I<sub>2</sub> m.  $150^{\circ}$ .<sup>482e</sup>  
 Pentamethylene, CH<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>Te, Cl<sub>2</sub> m.  $106^{\circ}$ ; Br<sub>2</sub> m.  $107^{\circ}$ ; I<sub>2</sub> m.  $136.5^{\circ}$ .<sup>224</sup>

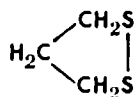
## TWO CARBONS, TWO SULFURS



- Me<sub>2</sub>C(S)<sub>2</sub>CMe<sub>2</sub>, b.  $182-5^{\circ}$ ,<sup>392</sup>  $183-5^{\circ}$ ; <sup>16</sup>, <sup>704</sup> disulfone, m.  $220-5^{\circ}$ .<sup>16</sup>  
 MeEtC(S)<sub>2</sub>CMeEt, b<sub>15</sub>  $120-30^{\circ}$ .<sup>392</sup>  
 Et<sub>2</sub>C(S)<sub>2</sub>CEt<sub>2</sub>, b<sub>15</sub>  $135-40^{\circ}$ .<sup>392</sup>  
 PhCH:CHC(Me)(S)<sub>2</sub>CMeCH:CHPh, m.  $132.5^{\circ}$ .<sup>249</sup>  
 Ph<sub>2</sub>C:C(S)<sub>2</sub>C:CPh<sub>2</sub>, m.  $258^{\circ}$ .<sup>606</sup>  
 Cl<sub>2</sub>C(S)<sub>2</sub>CCl<sub>2</sub>, m.  $119^{\circ}$ .<sup>603</sup>  
 Cl<sub>2</sub>C(S)<sub>2</sub>C:NPh, m.  $70^{\circ}$ .<sup>603</sup>  
 PhCOCH:C(S)<sub>2</sub>C:CHCOPh, m.  $214^{\circ}$ .<sup>366b</sup>  
 C<sub>4</sub>H<sub>3</sub>S•COCH:C(S)<sub>2</sub>C:CHCO•C<sub>4</sub>H<sub>3</sub>S, dec.  $260^{\circ}$ .<sup>366b</sup>  
 PhCOCMe:C(S)<sub>2</sub>C:CMeCOPh, m.  $225^{\circ}$ .<sup>366b</sup>  
 MeC<sub>6</sub>H<sub>4</sub>COCMe:C(S)<sub>2</sub>C:CMeCOC<sub>6</sub>H<sub>4</sub>Me, m.  $265^{\circ}$ .<sup>366b</sup>  
 C<sub>4</sub>H<sub>3</sub>S•COCMe:C(S)<sub>2</sub>C:CMeCO•C<sub>4</sub>H<sub>3</sub>S, m.  $260^{\circ}$ .<sup>366b</sup>  
 β-C<sub>10</sub>H<sub>7</sub>COCMe:C(S)<sub>2</sub>C:CMeCOC<sub>10</sub>H<sub>7</sub>-β, m.  $264^{\circ}$ .<sup>366b</sup>  
 S(CHMe)<sub>2</sub>S<sub>2</sub>, b<sub>14</sub>  $89-90^{\circ}$ .<sup>441b</sup>  
 S(CPh<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, m.  $124^{\circ}$ .<sup>639</sup>

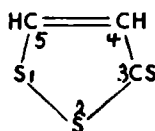
## THREE CARBONS, TWO SULFURS

## 1,2-Dithiolane



- 4,4-Dimethyl-,  $b_{17}$   $84-6^\circ$ ,  $b_{27}$   $128-9^\circ$ .<sup>34</sup>  
 4,4-Di(hydroxymethyl)-, m.  $130^\circ$ .<sup>531</sup>  
 4-Pentamethylene-,  $b_{17}$   $148^\circ$ ;  $\text{HgCl}_2$  m.  $91^\circ$ .<sup>34</sup>  
 3,5-Dicarboxy-, DL m.  $199^\circ$ ; D m.  $176-80^\circ$ ; L m.  $177-81^\circ$ .<sup>607a</sup>  
 4-Keto-, semicarbazone, m.  $224^\circ$ .<sup>607c</sup>  
 3-( $\delta$ -carboxybutyl)-, m.  $61^\circ$ ; <sup>126, 127</sup>  $b_{0.1}$   $160-5^\circ$ , <sup>127</sup>  $150^\circ$ .<sup>126</sup>  
 $\text{Me}_2\text{C}(\text{CH}_2)_2\text{S}_3$ ,  $b_{14}$   $117-8^\circ$ .<sup>34</sup>  
 $\text{Me}_2\text{C}(\text{CH}_2)_2\text{C}(\text{CH}_2)_2\text{S}_2$ ,  $b_{27}$   $128-9^\circ$ .<sup>29a</sup>  
 $\text{S}(\text{CH}_2)_2\text{C}(\text{CH}_2)_2\text{S}_2$ , m.  $56.5^\circ$ .<sup>29a</sup>  
 $\text{S}_2(\text{CH}_2)_2\text{C}(\text{CH}_2)_2\text{S}_2$ , m.  $80.5^\circ$ ;  $\text{HgCl}_2$   $132^\circ$ ;  $\text{HgBr}_2$   $127.5^\circ$ .<sup>29b</sup>  
 $\text{S}_2(\text{CH}_2)_2\text{C}(\text{CH}_2)_2\text{S}_3$ , m.  $118^\circ$ .<sup>29b</sup>  
 $\text{S}_3(\text{CH}_2)_2\text{C}(\text{CH}_2)_2\text{S}_3$ , m.  $182-4^\circ$ .<sup>29b</sup>

## Trithione



- Trithione, m.  $82^\circ$ ,<sup>151, 430</sup>  $80^\circ$ ; <sup>695</sup>  $\text{HgCl}_2$  m.  $219^\circ$ ;  $\text{MeI}$  m.  $175^\circ$ .<sup>151</sup>  
 4-Methyl-, m.  $41.5^\circ$ ,<sup>634</sup>  $40^\circ$ ; <sup>407, 646, 695</sup>  $b_{1.7}$   $110-2^\circ$ ; d 20/4 1.466;  
 $\text{MeI}$  m.  $175^\circ$ .<sup>634</sup>  
 5-Methyl-, m.  $33^\circ$ .<sup>407, 424, 695</sup>  
 4,5-Dimethyl-, m.  $97^\circ$ ,<sup>94, 695</sup>  $96^\circ$ ,<sup>428</sup>  $95.5^\circ$ ,<sup>117</sup>  $95.2^\circ$ ,<sup>613</sup>  $94.5^\circ$ ; <sup>49</sup>  
 oxime, m.  $180^\circ$ ; <sup>94</sup>  $\text{MeI}$  m.  $149.3^\circ$ .<sup>428</sup>  
 5-Methyl-4-butyl-, m.  $33^\circ$ .<sup>407</sup>  
 4-Methyl-5-*t*-butyl-, m.  $81.3^\circ$ ,<sup>634</sup>  $80^\circ$ ; <sup>644, 645</sup>  $b_5$   $175^\circ$ ; d 20/4  
 1.359; 2  $\text{MeI}$  adducts, m.  $149.5^\circ$  and  $149^\circ$ .<sup>634</sup>  
 5-Methyl-4-phenyl-, m.  $92^\circ$ .<sup>407</sup>  
 4-Methyl-5-phenyl-, m.  $104.8^\circ$ ,<sup>684</sup>  $104^\circ$ ; <sup>407, 424</sup>  $b_{1.5}$   $208-9^\circ$ ; <sup>684</sup>  
 d 20/4 1.450; <sup>684, 729</sup> crystal structure; <sup>729</sup>  $\text{HgBr}_2$  m.  $215.2^\circ$ ;  
 $\text{MeI}$  m.  $136^\circ$ .<sup>684</sup>  
 5-Methyl-4-*p*-Methoxyphenyl-, m.  $149^\circ$ .<sup>589</sup>  
 4-Methyl-5-carbomethoxy-, m.  $119^\circ$ .<sup>55</sup>  
 5-Ethyl-, m.  $96.5^\circ$ .<sup>117</sup>

- 4-Neopentyl-, m.  $87.3^{\circ}$ ,<sup>634</sup>  $87^{\circ}$ ; <sup>644, 645</sup>  $b_{1.7}$   $159^{\circ}$ ; d 20/4 1.177; MeI m.  $158^{\circ}$ .<sup>634</sup>
- 4-Methyl-5-thienyl-, m.  $90^{\circ}$ .<sup>426</sup>
- 4-Phenyl-, m.  $123^{\circ}$ ,<sup>94</sup>  $112^{\circ}$ ,<sup>230, 407</sup>  $122.8^{\circ}$ ; <sup>684</sup> oxime, m.  $175^{\circ}$ ,<sup>94</sup>  $172.5^{\circ}$ ; <sup>684</sup> MeI m.  $194^{\circ}$ .<sup>230</sup>
- 5-Phenyl-, m.  $127^{\circ}$ ,<sup>91, 93a</sup>  $126.2^{\circ}$ ,<sup>684</sup>  $126^{\circ}$ ,<sup>94, 407, 422, 424, 430</sup>  $126.5^{\circ}$ ; <sup>430</sup> HgBr<sub>2</sub> m.  $155^{\circ}$ ; <sup>684</sup> di MeI m.  $155^{\circ}$ ; oxime, m.  $139^{\circ}$ .<sup>684</sup>
- 5-*p*-Bromophenyl-, m.  $129^{\circ}$ .<sup>422</sup>
- 4,5-Diphenyl-, m.  $160.5^{\circ}$ ,<sup>684</sup>  $159.5^{\circ}$ ; <sup>430</sup> di MeI m.  $171.5^{\circ}$ .<sup>684</sup>
- 5-Phenyl-4-*p*-Methoxyphenyl-, m.  $168^{\circ}$ .<sup>589</sup>
- 4-Phenyl-5-carbomethoxy-, m.  $128^{\circ}$ .<sup>55</sup>
- 5-Phenyl-4-carboxy-, Me ester, m.  $99^{\circ}$ ; <sup>425</sup> Et ester, m.  $64^{\circ}$ .<sup>55</sup>
- 4-*p*-Toyl-, m.  $104^{\circ}$ ,<sup>589</sup>  $123^{\circ}$ ; MeI m.  $179^{\circ}$ .<sup>230</sup>
- 4-*p*-Ethylphenyl-, m.  $108^{\circ}$ ; MeI m.  $164^{\circ}$ .<sup>230</sup>
- 4-*p-t*-Butylphenyl-, m.  $146^{\circ}$ ; MeI m.  $161.5^{\circ}$ .<sup>230</sup>
- 4-*p-t*-Amylphenyl-, m.  $112^{\circ}$ ; MeI m.  $156^{\circ}$  with decomposition.<sup>230</sup>
- 4- $\alpha$ -Naphthyl-, m.  $198^{\circ}$ .<sup>589</sup>
- 5- $\alpha$ -Naphthyl-, m.  $105^{\circ}$ .<sup>93a</sup>
- 4,5-Trimethylene-, m.  $119^{\circ}$ .<sup>407, 424</sup>
- 4,5-Tetramethylene-, m.  $92^{\circ}$ ,<sup>424</sup>  $98^{\circ}$ .<sup>407</sup>
- 5-*p*-Hydroxyphenyl-, m.  $191^{\circ}$ ,<sup>55</sup>  $190.5^{\circ}$ ,<sup>93a</sup>  $189^{\circ}$ ,<sup>589</sup>  $188^{\circ}$ ; <sup>422</sup> Ac., m.  $145^{\circ}$ ; <sup>589</sup> MeI m.  $226^{\circ}$ .<sup>93a</sup>
- 5-*o*-Methoxyphenyl-, m.  $95.5^{\circ}$ .<sup>93a</sup>
- 5-*p*-Methoxyphenyl-, m.  $111^{\circ}$ ,<sup>94</sup>  $110.5^{\circ}$ ,<sup>430</sup>  $109^{\circ}$ ,<sup>93a, 261, 422</sup>  $108.5^{\circ}$ ; <sup>262, 263</sup> Cl<sub>2</sub> m.  $98^{\circ}$ ; Br<sub>2</sub> m.  $156^{\circ}$ ; I<sub>2</sub> m.  $164^{\circ}$ ; HgCl<sub>2</sub> m.  $220^{\circ}$ ; SbCl<sub>3</sub> m.  $132^{\circ}$ ; SnCl<sub>4</sub> m.  $185^{\circ}$ ; <sup>423</sup> oxime, m.  $170^{\circ}$ ; <sup>94</sup> MeI m.  $190^{\circ}$ ,<sup>93a</sup>  $189^{\circ}$ .<sup>94</sup>
- 4-*p*-Methoxyphenyl-, m.  $152^{\circ}$ .<sup>589</sup>
- 4-*p*-Methoxyphenyl, 5-carbomethoxy-, m.  $113^{\circ}$ .<sup>589</sup>
- 5-(3,4-Methoxyhydroxyphenyl)-, m.  $183^{\circ}$ .<sup>421</sup>
- 5-(3,4-Dimethoxyphenyl)-, m.  $127^{\circ}$ ; <sup>421</sup> HgCl<sub>2</sub> m.  $225^{\circ}$ ; SnCl<sub>4</sub> m.  $195^{\circ}$ .<sup>421</sup>
- 5-(3,4-CH<sub>2</sub>O<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-, m.  $195^{\circ}$ ; HgCl<sub>2</sub> m.  $240^{\circ}$ ; SnCl<sub>4</sub> m.  $230^{\circ}$ .<sup>421</sup>
- 5-(3,4-MeO(MeO<sub>2</sub>CCH<sub>2</sub>O)C<sub>6</sub>H<sub>3</sub>)-, m.  $159^{\circ}$ .<sup>425</sup>
- 5-*p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>-, m.  $208.5^{\circ}$ ,<sup>55</sup>  $204^{\circ}$ ,<sup>422</sup>  $201^{\circ}$ ; MeI m.  $208^{\circ}$ .<sup>93a</sup>
- 5-(2-C<sub>4</sub>H<sub>3</sub>O)-, m.  $112^{\circ}$ .<sup>93a</sup>
- 5-(2-C<sub>4</sub>H<sub>3</sub>S)-, m.  $128^{\circ}$ ,<sup>93a</sup>  $130^{\circ}$ .<sup>426</sup>
- Pinene-, m.  $106^{\circ}$ , MeI m.  $142^{\circ}$ ; oxime, m.  $123^{\circ}$ .<sup>94</sup>

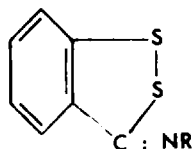
Benzotrithione, m.  $98^{\circ}$ ,<sup>407</sup> 437, 442  $95^{\circ}$ ,<sup>94</sup>  $90^{\circ}$ ; <sup>424</sup>  $\text{HgCl}_2$  m.  $225^{\circ}$ ; MeI m.  $140^{\circ}$ .<sup>94</sup>

5,4-(1,2-Naphthotrithione), m.  $170^{\circ}$ ; oxime, m.  $228^{\circ}$ .<sup>407</sup>

4,5-(2,3-Naphthotrithione), m.  $144^{\circ}$ ; oxime, m.  $232^{\circ}$ .<sup>407</sup>

4,5-(1,2-Naphthotrithione), m.  $149^{\circ}$ ; oxime, m.  $161^{\circ}$ .<sup>407</sup>

4,5-(1,8-Naphthotrithione), m.  $206^{\circ}$ .<sup>425</sup>



R=OH, m.  $208^{\circ}$ .

R=NH<sub>2</sub>, m.  $125^{\circ}$ .

OMe, m.  $55^{\circ}$ .

NHPh, m.  $106^{\circ}$ .

CH<sub>2</sub>CH<sub>2</sub>OH, m.  $107^{\circ}$ ; Ac. m.  $64.5^{\circ}$ .<sup>436</sup>

OCOPh, m.  $147^{\circ}$ .<sup>443</sup>

### Dithiones

5-Ph-, m.  $119^{\circ}$ ,<sup>91</sup>  $117^{\circ}$ .<sup>60, 430, 684</sup>

5-*p*-HOC<sub>6</sub>H<sub>5</sub>-, m.  $167^{\circ}$ ; Ac., m.  $147^{\circ}$ .<sup>589</sup>

5-*p*-MeOC<sub>6</sub>H<sub>5</sub>-, m.  $118.5^{\circ}$ ,<sup>430</sup>  $118^{\circ}$ ,<sup>421</sup>  $117^{\circ}$ ,<sup>91</sup>  $115^{\circ}$ .<sup>261, 262</sup>

5-(3,4(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-, m.  $124^{\circ}$ .<sup>421</sup>

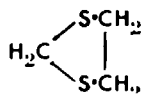
5-*p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>-, m.  $190^{\circ}$ .<sup>93a</sup>

5-(2-C<sub>4</sub>H<sub>9</sub>O)-, m.  $97^{\circ}$ .<sup>93a</sup>

5-(2-C<sub>4</sub>H<sub>9</sub>S)-, m.  $93^{\circ}$ .<sup>93a</sup>

Benzodithione, m.  $77^{\circ}$ ,<sup>627</sup>  $76^{\circ}$ .<sup>325</sup>

### 1,3-Dithiolane



Dithiolane, m.  $-51^{\circ}$ ; <sup>671</sup>  $b_{760}$   $175^{\circ}$ ,  $b_{11}$   $61^{\circ}$ ,<sup>270</sup>  $b_{14}$   $67^{\circ}$ ; <sup>151</sup>  $d_{17}$  1.259;  $n_{15/D}$  1.5975;  $\text{HgCl}_2$  m.  $119^{\circ}$ ,<sup>270</sup>  $126^{\circ}$ ; <sup>151</sup> MeI m.  $96^{\circ}$ ; monoxide,  $b_1$   $115-20^{\circ}$ , dioxide, m.  $134^{\circ}$ ; <sup>270</sup> disulfone, m.  $205^{\circ}$ ,<sup>62, 671</sup>  $224^{\circ}$ .<sup>270</sup>

2-Methyl-,  $b$   $172-3^{\circ}$ ,<sup>225</sup>  $b_{12}$   $58^{\circ}$ ; <sup>151</sup> disulfone, m.  $198^{\circ}$ .<sup>225</sup>

2-Methyl-2-carboxy-, m.  $102^{\circ}$ .<sup>225</sup>

2,2-Dimethyl-,  $b$   $171^{\circ}$ ; sulfone, m.  $232^{\circ}$ .<sup>225</sup>

2-Methyl-4-chloromethyl-,  $b_2$   $94^{\circ}$ .<sup>649</sup>

2-Methyl-2-hydroxymethyl-, m.  $58^{\circ}$ ;  $b_{0.8}$   $115^{\circ}$ .<sup>649</sup>

2-Methyl-2-ethyl-,  $b_3$   $55^{\circ}$ ;  $d_{25/4}$  1.0680;  $n_{25/D}$  1.5350.<sup>564</sup>

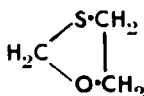
2-Methyl-2-*i*-propyl-,  $b_3$   $61^{\circ}$ ;  $d_{25/4}$  1.0511;  $n_{25/D}$  1.5302.<sup>564</sup>

2-Methyl-2-hexyl-,  $b_6$   $120^{\circ}$ ;  $d_{25/4}$  0.9926;  $n_{25/D}$  1.5110.<sup>564</sup>

2-Methyl-2-phenyl-,  $b_3$   $131^{\circ}$ ,<sup>564</sup>  $b_{11}$   $162-3.5^{\circ}$ ; <sup>318</sup>  $d_{25/4}$  1.1819;  $n_{25/D}$  1.6162.<sup>564</sup>

- 2,2-Dimethyl-4-chloromethyl-,  $b_{0.7}$   $80^\circ$ .<sup>649</sup>  
 2,2-Dimethyl-4-hydroxymethyl-, m.  $55^\circ$ ;  $b_1$   $105^\circ$ .<sup>649</sup>  
 2,2-Dimethyl-4-carboxy-, m.  $53^\circ$ ;  $b_{1.5}$   $121-2^\circ$ ; Me ester,  $b_{0.5}$   $73-4^\circ$ ; amide, m.  $90^\circ$ .<sup>398, 530</sup>  
 2,2-Dimethyl-4-butyl-,  $b_{12}$   $110^\circ$ ; n 22.5/D 1.5032.<sup>36</sup>  
 2-Ethyl-, b.  $191-2^\circ$ ; sulfone, m.  $124^\circ$ .<sup>225</sup>  
 2-Ethyl-2-butyl-,  $b_5$   $102^\circ$ ; d 25/4 1.0126; n 25/D 1.5191.<sup>564</sup>  
 2-Ethyl-2-phenyl-,  $b_2$   $135^\circ$ ; d 25/4 1.1542; n 25/D 1.6050.<sup>564</sup>  
 2,2-Dipropyl-,  $b_2$   $86^\circ$ ; d 25/4 1.0158; n 25/D 1.5200.<sup>564</sup>  
 2-Propyl-2-phenyl-,  $b_4$   $145^\circ$ ; d 25/4 1.1287; n 25/D 1.5915.<sup>564</sup>  
 2,2-Di-*i*-propyl, m.  $40^\circ$ ;  $b_4$   $94^\circ$ .<sup>564</sup>  
 2-Butyl-2-phenyl-,  $b_4$   $154^\circ$ ; d 25/4 1.1035; n 25/D 1.5830.<sup>564</sup>  
 2,2-Di-*i*-butyl-,  $b_6$   $115^\circ$ ; d 25/4 0.9892; n 25/D 1.5115.<sup>564</sup>  
 2-Amyl-2-phenyl-,  $b_4$   $169^\circ$ ; d 25/4 1.0838; n 25/D 1.5755.<sup>564</sup>  
 2-Phenyl-, m.  $29^\circ$ .<sup>225</sup>  
 2-Phenyl-4-chloromethyl, m.  $70^\circ$ ;  $b_{0.8}$   $150^\circ$ .<sup>649</sup>  
 2-Phenyl-4-hydroxymethyl-, m.  $77^\circ$ ;  $b_{1.5}$   $207^\circ$ .<sup>532, 649</sup>  
 2-Phenyl-4-cyanomethyl-, m.  $69^\circ$ ; b.  $180^\circ$ .<sup>649</sup>  
 2,2-Diphenyl-, m.  $106^\circ$ .<sup>225</sup>  
 2-Phenyl-2-benzoyl-, m.  $94.5^\circ$ .<sup>343</sup>  
 2-Styryl-4-carboxy-, m.  $100^\circ$ .<sup>571</sup>  
 2-Phenacyl-, m.  $80^\circ$ .<sup>366c</sup>  
 2-Thenacyl-, m.  $99^\circ$ .<sup>366c</sup>  
 2,2-Tetramethylene-,  $b_5$   $89^\circ$ ; d 25/4 1.1464; n 25/D 1.5679.<sup>564</sup>  
 2,2-Pentamethylene-,  $b_5$   $107^\circ$ ,<sup>564</sup>  $b_6$   $114-5^\circ$ ; <sup>317</sup> d 25/4 1.1288; n 25/D 1.5650.<sup>564</sup>  
 2,2-MeCH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C(SCH<sub>2</sub>)<sub>2</sub>,  $b_{13}$   $126^\circ$ ; d 25/4 1.0907; n 25/D 1.5478.<sup>564</sup>  
 2,2-Pentamethylene-4-hydroxymethyl-, m.  $70^\circ$ ;  $b_{0.8}$   $150^\circ$ .<sup>649</sup>  
 4,4,5,5-Tetraphenyl-, m.  $200^\circ$ .<sup>596</sup>  
 2-Carboxy-, m.  $90^\circ$ ,<sup>158</sup>  $150^\circ$ .<sup>367</sup>  
 ( $\cdot$ CH<sub>2</sub>S)<sub>2</sub>CHCH(SCH<sub>2</sub>)<sub>2</sub>, m.  $135.5^\circ$ ,<sup>545</sup>  $133^\circ$ .<sup>225</sup>  
 2-Methyl-2-acyl-4,5-benzo-, MeAcCS<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-, m.  $156^\circ$ .<sup>343</sup>  
 2-Methyl-2-acetonyl-4,5-benzo-, m.  $119^\circ$ .<sup>343</sup>  
 2-Phenyl-2-benzoyl-4,5-benzo-, m.  $175^\circ$ .<sup>343</sup>

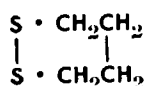
*1-Thia-3-oxacyclopentane*



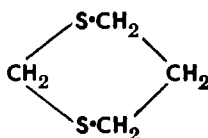


- 2 Methyl-4-keto-, m.  $145^{\circ}$ .<sup>395d</sup>  
 2 Methyl-2-carboxy-4 keto-, m.  $137^{\circ}$ .<sup>395b</sup>  
 2 *i*-Propyl-,  $b_{2.5} 29^{\circ}$ .<sup>373</sup>  
 2-Phenyl-,  $b_8 86-7^{\circ}$ .<sup>373</sup>  
 2-(3,4 CH<sub>2</sub>O<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-),  $b_{1.5} 118^{\circ}$ .<sup>373</sup>  
 2,2-Dimethyl-,  $b_{65} 70^{\circ}$ ;  $d_{24} 1.0105$ ;  $n_{25/D} 1.4742$ .<sup>197</sup>  
 2,2,4-Trimethyl-,  $b_{761} 141^{\circ}$ ;  $d_{20/4} 0.9782$ ;  $n_{20/D} 1.4645$ .<sup>624b</sup>  
 2,2-Dimethyl-4-chloromethyl-,  $b_{15} 75^{\circ}$ ;  $d_{20/4} 1.1567$ ;  $n_{20/D} 1.4940$ .<sup>624b</sup>  
 2,5-Dimethyl-4-keto-, m.  $108^{\circ}$ .<sup>395d</sup>  
 2 Methyl-2-ethyl-,  $b_8 42^{\circ}$ ;  $d_{24} 0.9776$ ;  $n_{25/D} 1.4751$ .<sup>197</sup>  
 2 Methyl-2-*i*-butyl-,  $b_2 41^{\circ}$ .<sup>197</sup>  
 2,2-Diethyl-4-keto-, m.  $81^{\circ}$ .<sup>395d</sup>  
 2,2-Pentamethylene-,  $b_{0.6} 47^{\circ}$ ,<sup>197</sup>  $b_{0.55} 51-3^{\circ}$ ;  $d_{25} 1.0781$ ;  $n_{25/D} 1.5119$ ,<sup>170.5</sup>  $1.5155$ .<sup>197</sup>  
 2,2-Dibenzyl-, m.  $43^{\circ}$ .<sup>197</sup>  
 2-Imino-, HCl m.  $121.5^{\circ}$ ,<sup>615</sup>  $121^{\circ}$ .<sup>616</sup>  
 $\text{Me}_2\text{C} \begin{array}{c} \diagup \text{SCH}_2 \\ \diagdown \text{OCH}_2 \end{array} \text{CH}_2$   $b_{12} 60^{\circ}$ ,<sup>624b</sup>  $b_{18} 49^{\circ}$ ;  $d_{24} 1.0216$ ,<sup>197</sup>  $d_{20/4} 1.0291$ ;  $n_{20/D} 1.4888$ ,<sup>624b</sup>  $n_{25/D} 1.4880$ .<sup>197</sup>

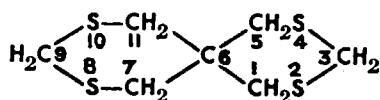
## FOUR CARBONS, TWO SULFURS

*1,2-Dithiane*

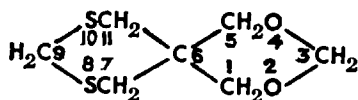
- 1,2-Dithiane, m.  $33^{\circ}$ ,<sup>53.7</sup>  $29^{\circ}$ ;  $111.5$   $b_4 58-63^{\circ}$ ,<sup>351</sup>  $b_{14} 80^{\circ}$ ,<sup>111.5</sup>  $b_{150} 82^{\circ}$ .<sup>53.7</sup>  
 3,6-Dimethyl-,  $b_{18} 66-9^{\circ}$ ;  $n_{25/D} 1.5461$ .<sup>133</sup>  
 3-( $\gamma$ -carboxypropyl)-, m.  $58^{\circ}$ ,<sup>126, 127</sup>  $62^{\circ}$ .<sup>561.5</sup>  
 3,6-Dicarboxy-, m.  $199^{\circ}$ .<sup>238d</sup>

*1,3-Dithiane*

- 1,3-Dithiane, m.  $53.5^{\circ}$ ,<sup>458</sup>  $54^{\circ}$ ; <sup>142</sup>, <sup>270</sup> b.  $207-8^{\circ}$ ; <sup>458</sup> disulfone, m.  $330^{\circ}$ ,<sup>270</sup>  $308^{\circ}$ .<sup>458</sup>
- 2-Methyl-, b<sub>5</sub>  $66^{\circ}$ ,<sup>142</sup> b<sub>9</sub>  $79-80^{\circ}$ ; disulfone, m.  $262^{\circ}$ ,<sup>20b</sup>  $264^{\circ}$ .<sup>142</sup>
- 2-Ethyl-, b<sub>5</sub>  $85^{\circ}$ ; <sup>142</sup> disulfone, m.  $209^{\circ}$ ,<sup>20b</sup>  $210^{\circ}$ .<sup>142</sup>
- 2-Propyl-, b<sub>5</sub>  $94^{\circ}$ ; disulfone, m.  $205^{\circ}$ .<sup>142</sup>
- 2,2-Dimethyl-, b<sub>5</sub>  $65^{\circ}$ ,<sup>142</sup> b<sub>9</sub>  $79-81^{\circ}$ ; disulfone, m.  $246^{\circ}$ .<sup>20b</sup>
- 2-Methyl-2-ethyl-, b<sub>5</sub>  $92^{\circ}$ ; disulfone, m.  $205^{\circ}$ .<sup>142</sup>
- 2-Methyl-2-propyl-, b<sub>5</sub>  $95^{\circ}$ ; disulfone, m.  $205^{\circ}$ .<sup>142</sup>
- 2-Methyl-2-propyl-, b<sub>5</sub>  $95^{\circ}$ ; disulfone, m.  $209^{\circ}$ .<sup>142</sup>
- 2,2-Diethyl-, b<sub>5</sub>  $85^{\circ}$ ; disulfone, m.  $201^{\circ}$ .<sup>142</sup>
- 2-Methyl-2-phenyl-, b<sub>5</sub>  $147^{\circ}$ .<sup>142</sup>
- 2-Methyl-2-benzyl-, disulfone, m.  $158^{\circ}$ .<sup>20b</sup>
- 2-Phenyl-, m.  $72^{\circ}$ ,<sup>493</sup>  $71^{\circ}$ ; <sup>20b</sup>, <sup>142</sup> disulfone, m.  $265^{\circ}$ .<sup>20b</sup>
- 2,2-Diphenyl-, m.  $110^{\circ}$ .<sup>142</sup>
- 2-Methyl-5,5-dihydroxy-, m.  $124^{\circ}$ ; disulfone, m.  $219^{\circ}$ .<sup>34</sup>
- 2,2-Dimethyl-5,5-dihydroxy-, m.  $200.5^{\circ}$ .<sup>34</sup>
- 2-Phenyl-2-benzoyl-, m.  $100^{\circ}$ .<sup>158</sup>
- 2-Phenyl-5-hydroxy-, m.  $143^{\circ}$ .<sup>649</sup>
- 2-Phenyl-5,5-dihydroxy-, m.  $211^{\circ}$ .<sup>34</sup>
- 2-Methyl-2-phenyl-5,5-dihydroxy-, m.  $165^{\circ}$ .<sup>34</sup>
- 2,2-Diphenyl-5,5-dihydroxy-, m.  $170^{\circ}$ .<sup>34</sup>
- 2-Carboxy-, m.  $116^{\circ}$ .<sup>158</sup>
- 5-Carboxy-, m.  $146-8^{\circ}$ .<sup>352, 353</sup>
- 2-Phenacylidene-, m.  $53^{\circ}$ .<sup>368a</sup>
- 4-Carbethoxy-5-keto-, m.  $62^{\circ}$ .<sup>152</sup>
- 2,2-Dimethyl-5,5-dimethyl-, m.  $58.5^{\circ}$ .<sup>34</sup>
- 2,2-Dimethyl-5,5-pentamethylene-, m.  $77^{\circ}$ ; disulfone, m.  $221^{\circ}$ .<sup>34</sup>
- 2,2-Dimethyl-5,5-di-(hydroxymethyl)-, m.  $200^{\circ}$ ; diAc., m.  $72^{\circ}$ .<sup>84</sup>
- 2-Methyl-2-ethyl-5,5-pentamethylene-, m.  $37.5^{\circ}$ .<sup>34</sup>
- 2-Methyl-2-phenyl-5,5-dimethyl-, m.  $60^{\circ}$ .<sup>34</sup>
- 2,2-Diphenyl-5,5-dimethyl-, m.  $90.5^{\circ}$ .<sup>34</sup>
- 2-Phenyl-5,5-pentamethylene-, m.  $162^{\circ}$ .<sup>34</sup>
- 2,2-Diphenyl-5,5-pentamethylene-, m.  $125^{\circ}$ .<sup>34</sup>
- 2,2-Tetramethylene-5,5-pentamethylene-, m.  $68.5^{\circ}$ .<sup>34</sup>
- 2,2-Pentamethylene-, m.  $41.5^{\circ}$ ; b<sub>17</sub>  $148-8.5^{\circ}$ .<sup>317</sup>
- 2,2-Pentamethylene-5,5-dihydroxy-, m.  $187.5^{\circ}$ .<sup>34</sup>
- 2,2-Pentamethylene-5,5-pentamethylene-, m.  $106.5^{\circ}$ .<sup>34</sup>
- 2-Furyl-5,5-dimethyl-, m.  $63.5^{\circ}$ .<sup>34</sup>
- 2-Furyl-5,5-pentamethylene-, m.  $103^{\circ}$ .<sup>34</sup>

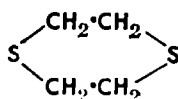


- 3,9-Dimethyl-, m.  $110^{\circ}$ .<sup>29c</sup>  
 3,9-Dimethyl-3,9-diacetyl-, m.  $165.5^{\circ}$ .<sup>29c</sup>  
 3,3,9,9-Tetramethyl-, m.  $193^{\circ}$ .<sup>29c</sup>  
 3,9-Dimethyl-3,9-diethyl-, m.  $143.5^{\circ}$ .<sup>29c</sup>  
 3,3,9,9-Tetraethyl-, m.  $118.5^{\circ}$ .<sup>29c</sup>  
 3,9-Dimethyl-3,9-di-*t*-butyl-, m.  $167^{\circ}$ .<sup>29c</sup>  
 3,9-Diethyl-3,9-di-*t*-butyl-, m.  $178^{\circ}$ .<sup>29c</sup>  
 3,3-Tetramethylene-9,9-tetramethylene-, m.  $213^{\circ}$ .<sup>29c</sup>  
 3,3-Pentamethylene-9,9-pentamethylene-, m.  $207^{\circ}$ .<sup>29c</sup>



- 3,3,9,9-Tetramethyl-, m.  $128^{\circ}$ .<sup>34</sup>  
 3,9-Dimethyl-3,9-diphenyl-, m.  $137^{\circ}$ .<sup>34</sup>  
 3,9-Diphenyl-, m.  $173.5^{\circ}$ .<sup>34</sup>

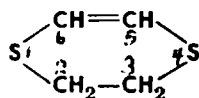
### 1,4-Dithiane



- 1,4-Dithiane, m.  $111^{\circ}$ ,<sup>159, 188, 344, 453, 671</sup>  $112^{\circ}$ ,<sup>11, 172a, 354, 445a</sup>  $113^{\circ}$ ,<sup>72, 552a</sup>  $110^{\circ}$ ,<sup>193, 264</sup>  $110.5^{\circ}$ ,<sup>721b</sup>  $109^{\circ}$ ,<sup>721a, 722</sup>  $108^{\circ}$ ,<sup>465a</sup>  $100^{\circ}$ ,<sup>418</sup>  
 b.  $200^{\circ}$ ,<sup>344, 453, 465a</sup>  $199$ – $200^{\circ}$ ,<sup>172a, 445a</sup>  $205^{\circ}$ ,<sup>193</sup>  $b_{60}$   $115.6^{\circ}$ ,  $b_{306}$   $163.7^{\circ}$ ;  $n_{20/D}$  1.4217;<sup>354</sup> MeCl m.  $225^{\circ}$ ; MeI m.  $175^{\circ}$ ,<sup>445b</sup>  $174^{\circ}$ ; <sup>11, 506</sup> di MeI m.  $208^{\circ}$ ; <sup>445b</sup> PhCH<sub>2</sub>Br m.  $146^{\circ}$ ; <sup>506</sup> mono-sulfone, m.  $200^{\circ}$ ; sulfoxide-sulfone, m.  $279^{\circ}$ ; disulfone, m.  $> 330^{\circ}$ .<sup>255</sup>  
 2-Methyl-, m.  $20^{\circ}$ ; b.  $209$ – $10^{\circ}$ ; <sup>458</sup> disulfone, m.  $304^{\circ}$ .<sup>259</sup>  
 2,6-Dimethyl-,  $b_{12}$   $85$ – $7^{\circ}$ ,<sup>274</sup>  $b_{18}$   $80$ – $100^{\circ}$ ; <sup>451.5</sup> d  $20/4$  1.078;  $n_{20/D}$  1.5420,<sup>274</sup> 1.5324; <sup>451.5</sup> monosulfone, m.  $146^{\circ}$ ; <sup>31, 451.5</sup> disulfone, m.  $320^{\circ}$ ,<sup>340</sup>  $313^{\circ}$ .<sup>451.5</sup>  
 2,5-Dimethyl-2,5-endoxy-, m.  $8^{\circ}$ ; <sup>338, 607a</sup>  $b_{0.2}$   $55$ – $6^{\circ}$ ,<sup>338</sup>  $b_{14}$   $96$ – $7^{\circ}$ .<sup>660</sup>  
 2,3,5,6-Tetramethyl-,  $b_{35}$   $145$ – $50^{\circ}$ .<sup>539</sup>  
 2,6-Dipropyl-,  $b_{20}$   $145$ – $55^{\circ}$ ; d  $20/4$  1.000;  $n_{20/D}$  1.5255.<sup>274</sup>  
 2,6-Diphenyl-,  $b_{30}$   $190$ – $5^{\circ}$ ; d  $20/4$  1.141;  $n_{20/D}$  1.6060.<sup>274</sup>

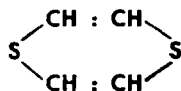
- 2,5-Diphenyl-2,5-diethylmercapto-, m. 161°. <sup>284</sup>  
 2,5-Dihydroxy-, m. 138–43°; diAc., m. 173°; diBz., m. 205°. <sup>322</sup>  
 2,5-Dimethoxy-, *cis-trans*, b<sub>1</sub> 79–84°; α-isomer, m. 85°. <sup>525</sup>  
 2-Ethoxy-, b<sub>8</sub> 88°; n 25/D 1.5410. <sup>519</sup>  
 2,5-Diethoxy-, m. 92°, <sup>525</sup> 91°; <sup>322</sup> b<sub>4</sub> 93–111°; α-isomer, m. 92°. <sup>525</sup>  
 2,5-Diketo-, m. 119.5°. <sup>593</sup>  
 2,5-Dicarboxy-, m. 110°; diEt ester, b<sub>20</sub> 62–3°. <sup>676</sup>  
 2-Hydroxymethyl-, b<sub>0.4</sub> 103–5°; n 20/D 1.5935, n 25/D 1.5910;  
 disulfone, m. 278°; Bz., m. 48.5°; b<sub>0.5</sub> 77°; *p*-nitro benzoate,  
 m. 97°. <sup>259</sup>  
 2-Chloromethyl-, b<sub>0.2</sub> 80–2°; d 20/4 1.312; n 25/D 1.5884; di-  
 sulfone, m. 255°. <sup>259</sup>  
 2,5-Dihydroxy-2,5-di(methylmercaptomethyl)-, m. 178°; diAc.,  
 m. 144°. <sup>607c</sup>

## 1,4-Dithiene



- 1,4-Dithiene, b<sub>29</sub> 101°; n 25/D 1.6273. <sup>519</sup>  
 2-Hydroxy-, Ac. b<sub>0.3</sub> 85–7°; b<sub>11</sub> 133–5°, b<sub>13</sub> 135–41°. <sup>322</sup>  
 2-Methoxy-, b<sub>4</sub> 63.1–3.2°; n 28.5/D 1.5942. <sup>525</sup>  
 2-Ethoxy-, b<sub>2</sub> 68–72°; n 25/D 1.5731. <sup>525</sup>  
 Benzo-, b<sub>0.18</sub> 82.5–5°; n 25/D 1.6713; disulfone, m. 222.5°. <sup>522</sup>  
 2-Ethoxybenzo-, b<sub>0.9</sub> 124–5°; n 25/D 1.6229; <sup>522, 576</sup> 1,3,5-trinitro-  
 benzene adduct, m. 104.5°. <sup>576</sup>

## Dithiadene



- Dithiadene, b<sub>17</sub> 77°; n 30/D 1.6319. <sup>525</sup>  
 2,5-Diphenyl-, m. 119°, <sup>89, 355, 523</sup> 118°, <sup>284</sup> 117°. <sup>46</sup>  
 3-Nitro-2,5-diphenyl-, m. 133. <sup>523</sup>  
 2,5-Dimethyl-3,6-diphenyl-, m. 138°. <sup>46</sup>  
 2,5-Di(*m*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)-, m. 222°. <sup>46</sup>  
 2,5-Di-*p*-tolyl-, m. 138°. <sup>355</sup>  
 2,5-Di-β-C<sub>10</sub>H<sub>7</sub>-, m. 200°. <sup>46</sup>  
 2,5-Dicarboxymethyl-, m. 140°; diEt ester, m. 168°. <sup>643</sup>

Benzo-, b.  $220^{\circ}$ ,  $b_{0.1}$   $67-70^{\circ}$ ;  $^{522, 576}$   $d_{20}$  1.2799;  $^{522}$   $n$  20/D 1.6760;  $^{576}$   $n$  25/D 1.6754;  $^{522, 576}$  1,3,5-trinitrobenzene adduct, m.  $98.5^{\circ}$ . $^{576}$

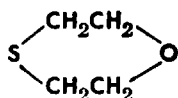
2-Nitrobenzo-, m.  $105.5^{\circ}$ ;  $^{522}$   $106^{\circ}$ . $^{576}$

2-Aldehydobenzo-, oxime, m.  $169^{\circ}$ . $^{522}$

2-Acetylbenzo-, m.  $55.5^{\circ}$ ;  $b_{0.08}$   $124-7^{\circ}$ ; oxime, m.  $170^{\circ}$ . $^{524}$

2-Carboxybenzo-, m.  $137^{\circ}$ . $^{524}$

### 1,4-Thioxane



Thioxane, m.  $-17^{\circ}$ ;  $^{354}$   $-19-18^{\circ}$ ;  $^{182}$  b.  $148.7^{\circ}$ ;  $^{354}$   $147^{\circ}$ ;  $^{159, 255}$   $b_{756}$   $145-8^{\circ}$ ;  $b_{740}$   $145.5-6.5^{\circ}$ ;  $^{721b}$   $b_{764}$   $148.9^{\circ}$ ;  $^{182}$   $b_{751}$   $145-6^{\circ}$ ;  $^{722}$   $b_{745}$   $144.5-5.5^{\circ}$ ;  $^{721a}$   $b_{47}$   $69.9^{\circ}$ ;  $b_{165}$   $100^{\circ}$ ;  $b_{549}$   $137.7^{\circ}$ ;  $^{354}$   $d$  15/4 1.1223;  $d$  20/4 1.11775;  $^{159}$  1.1171;  $^{182}$  1.1176;  $^{721b}$  1.1190;  $^{722}$  1.1143;  $^{721a}$   $n$  20/D 1.5081;  $^{354}$  1.5072;  $^{721b}$  1.5023;  $^{722}$  1.5070;  $^{721a}$  1.5066;  $^{721b}$   $Br_2$  m.  $85^{\circ}$ ;  $I_2$  m.  $67^{\circ}$ ;  $EtI$  m.  $85^{\circ}$ ;  $^{255}$   $HgCl_2$  m.  $171^{\circ}$ ;  $^{159}$   $167^{\circ}$ ;  $^{721a}$  sulfoxide, m.  $45^{\circ}$ ;  $^{255}$   $25^{\circ}$ ;  $^{148}$   $b_{15}$   $147^{\circ}$ ;  $^{148, 255}$  sulfone, m.  $130^{\circ}$ ;  $^{62, 255}$   $105.5^{\circ}$ . $^{451.5}$

5-Methyl-3-ethoxy-,  $b_{14}$   $88^{\circ}$ ;  $n$  20/D 1.4750. $^{517}$

3,5-Dimethyl-, b.  $162^{\circ}$ ; sulfone, m.  $102^{\circ}$ . $^{340}$

2,6-Dimethyl-, b.  $160-1^{\circ}$ ;  $^{451.5}$   $b_{16}$   $113-4^{\circ}$ ;  $n$  20/D 1.4748;  $^{298}$  1.4733; sulfone, m.  $105.5^{\circ}$ . $^{451.5}$

2,3-Dimethyl, 3-ethoxy-,  $b_{22}$   $68^{\circ}$ ;  $n$  25/D 1.5183. $^{519}$

2,3-Dimethyl, 3-acetyl-,  $b_1$   $83-4^{\circ}$ ;  $n$  20/D 1.4758. $^{519}$

5,5-Dimethyl, 3-ethoxy-,  $b_{12}$   $87^{\circ}$ ;  $n$  25/D 1.4732. $^{517}$

5,5-Dimethyl, 3-butoxy-,  $b_{13}$   $119^{\circ}$ ;  $n$  20/D 1.4700. $^{517}$

2,2,6,6-Tetramethyl-,  $b_{19}$   $130-2^{\circ}$ ;  $n$  20/D 1.4748. $^{298}$

3,5-Dihydroxy-, m.  $73^{\circ}$ . $^{164}$

3-Methoxy-,  $b_5$   $57^{\circ}$ ;  $b_{20}$   $85^{\circ}$ ;  $^{518}$   $b_{23}$   $85^{\circ}$ ;  $^{519}$   $b_{30}$   $92^{\circ}$ ;  $^{517}$   $n$  20/D 1.4941;  $^{519}$  1.4922;  $^{517}$   $n$  23/D 1.4911. $^{518}$

3-Ethoxy-,  $b_{14}$   $81-2^{\circ}$ ;  $n$  20/D 1.4850. $^{517}$

3,5-Diethoxy-, m.  $101^{\circ}$ . $^{160}$

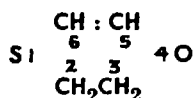
3-Butoxy-,  $b_{13}$   $109^{\circ}$ . $^{517}$

3,5-Diketo-, m.  $102^{\circ}$ ;  $^{7.5}$   $101^{\circ}$ ;  $^{394.5}$   $b_{10}$   $158^{\circ}$ ;  $^{7.5}$   $b_{12}$   $158-9^{\circ}$ . $^{394.5}$

2,6-Dimethyl-3,5-diketo-,  $b_{14}$   $133-7^{\circ}$ ;  $n$  20/D 1.5010. $^{394.5}$

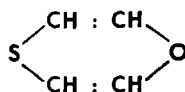
2,6-Diethyl-3,5-diketo-, m.  $15^{\circ}$ ;  $b_{15}$   $149-50^{\circ}$ ;  $n$  20/D 1.4942. $^{394.5}$

## Thioxene



Thioxene,  $b_5$   $60^\circ$ ,<sup>519</sup>  $b_{20}$   $54^\circ$ ;  $n$  20.7/D 1.5357,<sup>518</sup> 1.5208.<sup>519</sup>  
 2,3-Dimethyl-,  $b_{22}$   $68^\circ$ ;  $n$  25/D 1.5183.<sup>519</sup>  
 3-Ethoxybenzo-,  $b_4$   $125^\circ$ ;  $n$  20.5/D 1.5732,  $n$  25/D 1.5713.<sup>520</sup>  
 3-Butoxybenzo-,  $b_{0.25}$   $95-6^\circ$ ;  $n$  23/D 1.5498.<sup>520</sup>  
 3-Hydroxybenzo-,  $m$ .  $62.5^\circ$ ; Ac.,  $m$ .  $55.5^\circ$ .<sup>520</sup>  
 Dibenzo-2,2'-ether,  $m$ .  $120^\circ$ .<sup>520</sup>  
 2,3-Dibromobenzo-,  $m$ .  $106^\circ$ .<sup>520</sup>

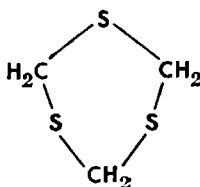
## Thioxadiene



Benzo-,  $b_{0.48}$   $49^\circ$ ;  $n$  25/D 1.6129.<sup>520</sup>

## THREE CARBONS, THREE SULFURS

## Trithiane



Trithiane,  $(\text{CH}_2\text{S})_3$ ,  $m$ .  $216^\circ$ ,<sup>15b, 203, 254, 324a, 324b, 324c, 327d, 569, 673,</sup>  
<sup>706</sup>  $215^\circ$ ,<sup>472</sup>  $217^\circ$ ,<sup>588</sup>  $218^\circ$ .<sup>267, 327b, 327e, 445a, 470e, 673</sup>

Trithioacetaldehyde,  $(\text{CH}_3\text{CHS})_3$ ,  $\alpha$ - $m$ .  $101^\circ$ ,<sup>21, 59a, 203, 248, 349a,</sup>  
<sup>374c, 500, 706</sup>  $102^\circ$ ,<sup>56b, 58b, 214</sup>  $98^\circ$ ,<sup>500</sup>  $90^\circ$ ; <sup>172a</sup>  $d$  20/4 1.178;<sup>21</sup>  
 $\beta$ - $m$ .  $126^\circ$ ,<sup>21, 58b, 203, 441c, 622</sup>  $125^\circ$ ,<sup>56b, 59a, 500, 706</sup>  $124^\circ$ ; <sup>374a</sup>  
 $b$ .  $247^\circ$ ,<sup>186e, 187b</sup>  $246-7^\circ$ ,<sup>374c</sup>  $245-8^\circ$ ,<sup>374a</sup>  $249^\circ$ ,<sup>214</sup>  $242^\circ$ ,<sup>446a</sup>  
 $205^\circ$ ; <sup>172a</sup>  $d$  20/4 1.150.<sup>21</sup>

2,4,6-Trichloro-trithioacetaldehyde,  $(\text{MeClCS})_3$ ,  $b_{10}$   $85-7^\circ$ .<sup>229</sup>

Trithiopropionaldehyde,  $(\text{EtCHS})_3$ ,  $m$ .  $36^\circ$  and  $76^\circ$ ;  $b_{10}$   $143^\circ$ ;  
 $n$  25/D 1.5472.<sup>200</sup>

Trithioallylaldehyde,  $(\text{CH}_2:\text{CHCH}_2\text{CHS})_3$ , trisulfone,  $m$ .  $267^\circ$ .<sup>420</sup>

Trithiofurfural,  $(\text{C}_4\text{H}_3\text{O}\cdot\text{CHS})_3$ ,  $\alpha$ - $m$ .  $128^\circ$ ,<sup>59e, 706</sup>  $95-8^\circ$ ; <sup>460</sup>  $\beta$ - $m$ .  
 $229^\circ$ .<sup>59e, 706</sup>

- Trithiobenzaldehyde,  $(\text{PhCHS})_3$ ,  $\alpha$ -m.  $167^\circ$ ,<sup>59a, 706</sup>  $164^\circ$ ,<sup>253</sup>  $164-7^\circ$ ;<sup>50, 133</sup>  $\beta$ -m.  $224^\circ$ ,<sup>93b</sup>  $225^\circ$ ,<sup>59a, 374b, 706</sup>  $226^\circ$ ,<sup>58b, 253, 323b, 374a, 470c</sup>  $228^\circ$ .<sup>133</sup>
- Trithiophenylacetaldehyde,  $(\text{PhCH}_2\text{CHS})_3$ ,  $\alpha$ -m.  $123^\circ$ ;  $\beta$ -m.  $169^\circ$ .<sup>199</sup>
- Trithiocinnamaldehyde,  $(\text{PhCH:CHCHS})_3$ ,  $\alpha$ -m.  $167^\circ$ ;  $\beta$ -m.  $213^\circ$ .<sup>59a, 59c</sup>
- Trithio-*m*-tolualdehyde,  $\alpha$ -m.  $144^\circ$ ;  $\beta$ -m.  $225^\circ$ .<sup>706</sup>
- Trithio-*p*-tolualdehyde,  $\alpha$ -m.  $150^\circ$ ;  $\beta$ -m.  $180^\circ$ .<sup>706</sup>
- Trithiomesitaldehyde, m.  $187^\circ$ .<sup>258</sup>
- Trithioanisaldheyde,  $\alpha$ -m.  $127^\circ$ ;  $\beta$ -m.  $183^\circ$ ,<sup>59a, 59c</sup>  $186^\circ$ ,<sup>470c</sup>  $180^\circ$ .<sup>93b</sup>
- Trithiosalicylaldehyde,  $\beta$ -m.  $210^\circ$ .<sup>383</sup>
- Trithio-*m*-hydroxybenzaldehyde,  $\beta$ -m.  $212^\circ$ .<sup>383</sup>
- Trithio-*p*-hydroxybenzaldehyde,  $\beta$ -m.  $215^\circ$ .<sup>383</sup>
- Trithiomethylsalicylaldehyde,  $\alpha$ -m.  $157^\circ$ ;  $\beta$ -m.  $224^\circ$ .<sup>59a, 59c</sup>
- Trithiomethyl-*m*-hydroxybenzaldehyde,  $\beta$ -m.  $147^\circ$ .<sup>383</sup>
- Trithio-*i*-butylsalicylaldehyde,  $\alpha$ -m.  $142^\circ$ ;  $\beta$ -m.  $150^\circ$ .<sup>59a, 59c</sup>
- Trithio-*o*-chlorobenzaldehyde,  $\alpha$ -m.  $163.5^\circ$ ;  $\beta$ -m.  $224.6^\circ$ .<sup>638</sup>
- Trithio-*m*-chlorobenzaldehyde,  $\alpha$ -m.  $116.4^\circ$ ;  $\beta$ -m.  $163.2^\circ$ .<sup>638</sup>
- Trithio-*p*-chlorobenzaldehyde,  $\alpha$ -m.  $138.2^\circ$ ;  $\beta$ -m.  $190.4^\circ$ .<sup>638</sup>
- Trithio-*o*-bromobenzaldehyde,  $\alpha$ -m.  $186.7^\circ$ ;  $\beta$ -m.  $221.0^\circ$ .<sup>638</sup>
- Trithio-*m*-bromobenzaldehyde,  $\alpha$ -m.  $142.3^\circ$ ;  $\beta$ -m.  $177.9^\circ$ .<sup>638</sup>
- Trithio-*p*-bromobenzaldehyde,  $\alpha$ -m.  $183.0^\circ$ ;  $\beta$ -m.  $205.9^\circ$ .<sup>638</sup>
- Trithio-*o*-iodobenzaldehyde,  $\alpha$ -m.  $189.6^\circ$ ;  $\beta$ -m.  $202.6^\circ$ .<sup>638</sup>
- Trithio-*m*-iodobenzaldehyde,  $\alpha$ -m.  $197.4^\circ$ ;  $\beta$ -m.  $213^\circ$ .<sup>638</sup>
- Trithio-*p*-iodobenzaldehyde,  $\alpha$ -m.  $114.8^\circ$ ;  $\beta$ -m.  $212^\circ$ .<sup>638</sup>
- Triselenane,  $(\text{CH}_2\text{Se})_3$ , m.  $210^\circ$ .<sup>111</sup>
- Trithioacetone, m.  $24^\circ$ ,<sup>89, 247, 469</sup>  $22^\circ$ ,<sup>21</sup>  $b_{10}$   $105-7^\circ$ ,<sup>200</sup>  $b_{15}$   $116-7^\circ$ ,<sup>89</sup>  $b_{13}$   $130^\circ$ , b.  $225-30^\circ$ ; <sup>247</sup> d  $20/4$  1.068; <sup>21</sup> n  $24/D$  1.5400; <sup>200</sup> trisulfone, m.  $302^\circ$ .<sup>58a, 58b, 469</sup>
- Trithiobutanone,  $b_{175}$   $238^\circ$ ;  $d_{20}$  1.03; <sup>112</sup> trisulfone, m.  $269^\circ$ .<sup>420</sup>
- Trithiocyclopentanone, m.  $99.1^\circ$ ; <sup>246b</sup>  $b_{10}$   $86-8^\circ$ ; <sup>614</sup> trisulfone, m.  $172^\circ$ .<sup>246b</sup>
- Trithiocyclohexanone, m.  $102^\circ$ ; <sup>246b</sup>  $b_{15}$   $76^\circ$ .<sup>614</sup>
- Trithioacetophenone, m.  $122.1^\circ$ ,<sup>58c, 93b, 163, 199</sup>  $119.5^\circ$ ; <sup>212</sup>  $b_{20}$   $110^\circ$ .<sup>470a</sup>

## MISCELLANEOUS CYCLICS

- 4,8-Thioctic acid, m.  $86^\circ$ .<sup>126, 127</sup>
- 1,2-Dithiacycloheptane-3,7-dicarboxylic acid, m.  $194^\circ$ .<sup>607d</sup>

$\text{CH}_2(\text{CH}_2\text{SCH}_2)_2$ , m.  $47^\circ$ ; <sup>458, 671</sup> b.  $221-2^\circ$ ; <sup>458</sup> disulfone, m.  $282^\circ$ ; <sup>20b</sup>  $288^\circ$ . <sup>458</sup>

$\text{HOCH}(\text{CH}_2\text{SCH}_2)_2$ , m.  $65.5^\circ$ ; benzoate, m.  $76^\circ$ . <sup>259</sup>

$\text{S}(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$ , m.  $-15^\circ$ ; b.  $245-6^\circ$ ; disulfone, m.  $258^\circ$ ; <sup>458</sup>  $259^\circ$ . <sup>20b</sup>

$\text{S}(\text{CMe}_2\text{COCMe}_2)_2\text{S}$ , m.  $104-6^\circ$ . <sup>607b</sup>

$\text{CH}_2(\text{CH}_2\text{SCH}_2\text{CH}_2)_2$ , m.  $57.5^\circ$ ; sublimes,  $260^\circ$ ; disulfone, m.  $185.6^\circ$ . <sup>458</sup>

$(\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2)_2$ , m.  $65^\circ$ . <sup>671</sup>

$\text{CH}_2(\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2)_2\text{CH}_2$ , m.  $122^\circ$ . <sup>671</sup>

$\text{CH}_2(\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2)_2\text{CH}_2$ , m.  $46^\circ$ . <sup>458</sup>

$(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2)_2$ , m.  $73^\circ$ . <sup>671</sup>

$(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2)_2$ , m.  $61^\circ$ . <sup>458</sup>

$(\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2)_2$ , m.  $62^\circ$ ; disulfone,  $261^\circ$ . <sup>458</sup>

$\text{CH}_2(\text{CH}_2\text{CH}_2\text{SCMe}_2\text{SCH}_2\text{CH}_2)_2\text{CH}_2$ , m.  $118^\circ$ . <sup>18</sup>

$\text{CH}_2(\text{CH}_2\text{CH}_2\text{SCEt}_2\text{SCH}_2\text{CH}_2)_2\text{CH}_2$ , m.  $113^\circ$ . <sup>18</sup>

$\text{CH}_2(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2)_2\text{CH}_2$ , m.  $89^\circ$ . <sup>671</sup>

$\text{S}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2)_2\text{S}$ , m.  $90^\circ$ ; sulfone, m.  $> 330^\circ$ . <sup>458</sup>

$\text{O}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2)_2\text{O}$ , m.  $125^\circ$ ; sulfone, m.  $266^\circ$ . <sup>458</sup>

*m*- $\text{C}_6\text{H}_4(\text{CH}_2\text{SCMe}_2\text{SCH}_2)_2\text{C}_6\text{H}_4$ , m.  $254^\circ$ ; sulfone, m.  $> 300^\circ$ . <sup>17</sup>

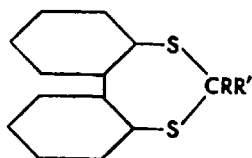
*p*- $\text{C}_6\text{H}_4(\text{CH}_2\text{SCHPhSCH}_2)_2\text{C}_6\text{H}_4$ , m.  $249^\circ$ . <sup>17</sup>

*p*- $\text{C}_6\text{H}_4[\text{CH}_2\text{SCH}(\text{C}_6\text{H}_4\text{Me-}m)\text{SCH}_2]_2\text{C}_6\text{H}_4$ , m.  $220^\circ$ . <sup>17</sup>

*p*- $\text{C}_6\text{H}_4[\text{CH}_2\text{SCH}(\text{C}_6\text{H}_4\text{Me-}p)\text{SCH}_2]_2\text{C}_6\text{H}_4$ , m.  $266^\circ$ . <sup>17</sup>

*o*- $\text{C}_6\text{H}_4(\text{CH}_2\text{S})_2\text{CH}_2$ , m.  $153^\circ$ . <sup>19b</sup>

*o*- $\text{C}_6\text{H}_4(\text{CH}_2\text{S})_2\text{CHMe}$ , m.  $110^\circ$ . <sup>19b</sup>



$\text{R \& R'} = \text{Me}$ , m.  $95^\circ$ . <sup>51</sup>

$\text{R} = \text{H}$ ,  $\text{R'} = \text{Ph}$ , m.  $106^\circ$ . <sup>51</sup>

$\text{R} = \text{Ph}$ ,  $\text{R'} = \text{PhCO}$ , m.  $198^\circ$ . <sup>51</sup>

$\text{PhCH}[\text{S}(\text{CH}_2)_{10}\text{S}]_2\text{CHPh}$ , m.  $135.8^\circ$ . <sup>451</sup>

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## CHAPTER 2.

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# Thials and Thiones

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### *Thioaldehydes and Thioketones*



### **General**

Formally, these have the same relation to aldehydes and ketones,  $\text{RCHO}$  and  $\text{RCOR}'$ , as mercaptans and thioethers do to alcohols and ethers:



Here, as elsewhere, the formulae of compounds containing bivalent sulfur are similar to those with bivalent oxygen. In some of their reactions there is close analogy between the oxygen and sulfur compounds but there is usually a marked difference in degree. Thus mercaptans can be esterified but the rates and limits are low as compared to those of the alcohols. The striking difference between thioaldehydes and thioketones is in the matter of the formation of cyclic trimers. Acetaldehyde can be converted to the cyclic paraldehyde; thioacetaldehyde is known only as the cyclic trimer. The trimer of acetone and the monomer of thioacetone are unknown. These statements apply specifically to the aliphatics; monomers are known among the aromatics. The formation and some of the reactions of thials and thiones will be considered here but the trimeric trithioaldehydes and

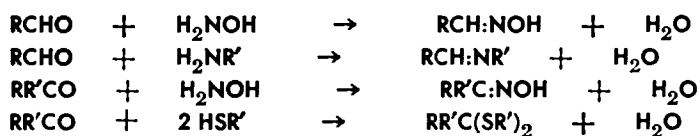
trithioketones are actually cyclic sulfides and for that reason have been taken up in chapter 1 on Cyclic Sulfides.

Aromatic ketones may appear as monomers or trimers according to the number and structure of the aryls present. Thioacetophenone can be obtained as a monomer which readily polymerizes to the trimer. Thiobenzophenone is monomeric and cannot be made to polymerize. The few aliphatic thioketones that have been isolated are from ketones that tend to enolize.<sup>35</sup>

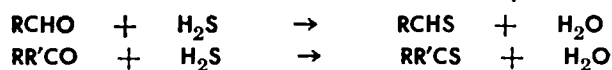
The aromatic thioaldehydes and thioketones differ from their oxygen analogs in being highly colored. This is true even of the monomeric ones. The :C:S group is a strong chromophore.<sup>37</sup>

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Kekulé imagined that alcohols could be changed into mercaptans and ethers into thio ethers by treatment with phosphorus pentasulfide, but was sadly mistaken. The oxygen of an alcohol (except a tertiary) is not readily removed and can not be taken out of the molecule without bringing the hydroxyl hydrogen with it. The oxygen in an ether is bound to two carbons and can not be disturbed without breaking up the molecule. There are a few apparent exceptions to this. On the other hand, a carbonyl oxygen can be exchanged for other atoms, or groups, without interfering with the rest of the molecule. This is characteristic of many aldehyde and ketone reactions:



In accordance with this the most general method of preparing thioaldehydes and thioketones, is the direct replacement of the oxygen of an aldehyde or ketone by sulfur. Hydrogen sulfide is the most frequently employed reagent.



These reactions take place in the presence of hydrochloric acid which is the preferred catalyst for the reactions of aldehydes and ketones with mercaptans.<sup>35</sup>

An ably written, comprehensive review of the chemistry of thiones and thials by Campaigne has appeared recently.<sup>39b</sup> This covers the preparation, properties, and reactions of all classes.



An earlier review on thioketones by Schönberg put great emphasis on the resemblances between monomeric thioketones such as thiobenzophenone and free radicals such as triphenylmethyl. Hexamethylethane is perfectly stable while if the methyls are replaced by phenyl groups, until hexaphenylethane is reached, the molecule tends to break in two.<sup>170a</sup> These reviews have been of great assistance in writing this chapter.

## Thioaldehydes

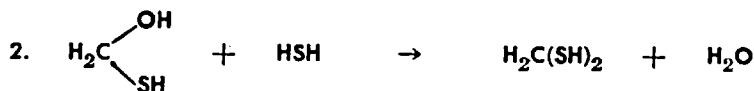
### TRITHIOFORMALDEHYDE

Trithioformaldehyde seems to have been obtained for the first time by the action of hydrogen sulfide on heated lead formate.<sup>217</sup> The yields were poor and the product sometimes contained oxygen and had a low melting point.<sup>91, 121</sup> The pyrolysis of lead formate gives formaldehyde which reacts more or less completely with the hydrogen sulfide.<sup>5</sup> Thioformaldehyde is formed by the reduction of an alkyl<sup>87a</sup> or aryl<sup>82</sup> isothiocyanate. Carbon disulfide is reduced to thioformaldehyde by zinc and an acid.<sup>73, 76</sup> It has been shown that methylene dimercaptan is formed in this reduction:<sup>136</sup>

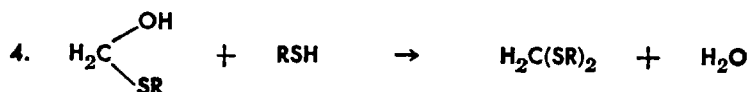


As will be shown later, this mercaptan is an intermediate product in the usual preparation of thioformaldehyde.

When formalin is mixed with twice its volume of concentrated hydrochloric acid and saturated with hydrogen sulfide, trithiane is precipitated.<sup>34.5, 54b, 75, 87b, 87c, 162</sup> The yield may be as high as 94%.<sup>29</sup> The primary reactions may be written:



The formation of mercaptals is well known:



Strong acids catalyze the formation of thioaldehydes and mercaptals. Methylene mercaptan,  $\text{HSCH}_2\text{SH}$ , may be expected to react with formaldehyde:



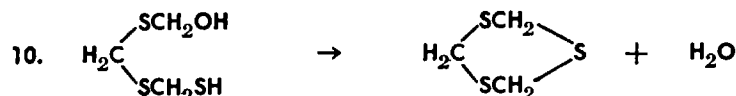
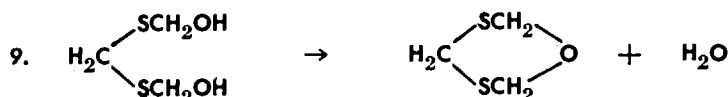
This should react with hydrogen sulfide:



Further reaction of the products of reactions 5 and 6 with formaldehyde would produce longer chains.



The elimination of water from these would produce cyclic compounds:



This is in accordance with the general tendency for six membered rings to form when possible. If cyclization does not take place these chains will continue to lengthen by reacting with additional formaldehyde and hydrogen sulfide. As the formation of rings with more than six members is unlikely, linear polymers will result. As is true of linear polymers in general, these will be mixtures of chains of all possible lengths.

The reactive intermediates postulated above cannot be isolated but the presence of  $\text{HSCH}_2\text{SCH}_2\text{SH}$  has been proved by alkylating it to the relatively stable tris-sulfide,  $\text{MeSCH}_2\text{SCH}_2\text{SMe}$ , and of  $\text{H}_2\text{C}(\text{SCH}_2\text{SH})_2$  by oxidising it to the disulfide,  $\text{CH}_2(\text{SCH}_2\text{S})_2$ .<sup>11a, 11b, 13d</sup>

Actually a number of products have been described resulting from the reaction of hydrogen sulfide and formaldehyde.<sup>11a</sup> In neutral solution a product corresponding to the formula,  $(\text{CH}_2\text{S})_3\text{CH}_2\text{O}$  has been obtained.<sup>54a</sup> A highly insoluble amorphous powder, melting at  $175-6^\circ$ , and having the composition,  $(\text{CH}_2\text{S})_n$ , has been isolated and also a dimercaptan,  $\text{HS}(\text{CH}_2\text{S})_n\text{H}$ .<sup>68, 219</sup> Just which of these will be formed depends on conditions, the

most important of which is the pH of the solution, the lower this is the more cyclization.<sup>68</sup> The preparation of thioformaldehyde at pH above 8.8 is claimed in a patent.<sup>224</sup>

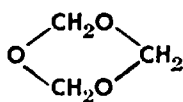
When  $n$  is large the composition does not vary greatly from one member to the next in the series,  $\text{HS}(\text{CH}_2\text{S})_n\text{H}$ , and tends to that of  $(\text{CH}_2\text{S})_n$ . Even if one sulfur atom is replaced by an oxygen the change is small. This is illustrated by the figures in table 2.1.

TABLE 2.1  
*Percentage Composition of Various Polymers*

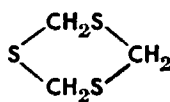
	$\text{HS}(\text{CH}_2\text{S})_{10}\text{H}$	$\text{HS}(\text{CH}_2\text{S})_{11}\text{H}$	$\text{HS}(\text{CH}_2\text{S})_{20}\text{H}$
C	24.26	24.43	25.12
S	71.27	71.10	70.42
H	4.46	4.47	4.45
	$\text{HS}(\text{CH}_2\text{S})_{21}\text{H}$	$(\text{CH}_2\text{S})_n$	$\text{HO}(\text{CH}_2\text{S})_{21}\text{H}$
C	25.17	26.05	25.58
S	70.40	69.56	68.30
H	4.43	4.38	4.50

Thioformaldehyde contrasts sharply with formaldehyde in that the tendency to form the cyclic trimer in preference to a linear polymer is so much greater. With formaldehyde linear polymerization is the rule; much of the Greek alphabet has been used up in naming brackets of formaldehyde polymers, which may be considered as having the general formula  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ . Where  $n$  is large it is impossible to distinguish between  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$  and  $(\text{CH}_2\text{O})_n$ . There is always uncertainty as to whether the water present is actually a part of the molecule or is only adsorbed. These polymers change progressively in properties as  $n$  increases up to 5000 in the so-called *eu*-polyoxymethylenes. The cyclic trioxymethylene has been known since 1885 but it was as late as 1942 that a practical method of preparation was developed.<sup>211</sup>

The facility with which thioformaldehyde trimerizes is all the more remarkable when the structural formulae of trioxane and trithiane are contrasted:



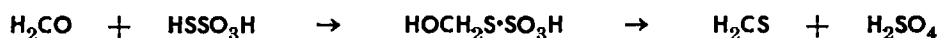
Trioxane



Trithiane

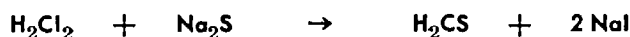
It has been pointed out in the chapter on Cyclic Sulfides that pentamethylene sulfide,  $(\text{CH}_2)_5\text{S}$ , is obtained in much poorer yields than tetramethylene sulfide,  $(\text{CH}_2)_4\text{S}$ , under comparable conditions. Dithiane,  $\text{S}(\text{CH}_2\text{CH}_2)_2\text{S}$ , is not prepared as readily as thioxane,  $\text{O}(\text{CH}_2\text{CH}_2)_2\text{S}$ . If the sulfur atom is considered to be spatially equivalent to  $-\text{CH}:\text{CH}-$ , as it appears to be in thiophene, pentamethylene sulfide would be more like a seven-membered ring and dithiane more like an eight-membered ring, which would explain the lower yields. According to this reasoning three sulfur atoms should take up the space of six carbon atoms which would make trithiane a nine-membered ring, the formation of which would seem to be unlikely. The trioxane ring is not planar; the trithiane ring would not be expected to be planar.

A convenient method of preparation which avoids the use of hydrogen sulfide is the acidification of a mixture of formalin and sodium thiosulfate.<sup>34,5, 86, 139, 169, 208a, 208b, 209a, 209b</sup> The sodium thiosulfate is fused, and 100 g. is mixed with 100 g. of 37% formaldehyde. This mixture is poured into 100 g. of conc. hydrochloric acid. The formaldehyde and thiosulfuric acid form a compound which breaks up: <sup>169, 209a, 209b</sup>



That the monomer is an intermediate is evidenced by the fact that a terrific odor is sometimes noticed.<sup>132,5</sup> The thioformaldehyde polymerizes to the insoluble trimer which separates out, allowing the reaction to go to completion. The trithioformaldehyde is filtered off and recrystallized from benzene.<sup>208a, 208b, 209a, 209b</sup>

Trithiane results also from the reaction of methylene iodide with sodium sulfide: <sup>87b, 92, 129</sup>



Artificial protein filaments are strengthened by insolubilizing them with nascent thioformaldehyde.<sup>194</sup>

Triselenane,  $(\text{CH}_2\text{Se})_3$ , m.  $210^\circ$ , has been prepared from formaldehyde and hydrogen selenide.<sup>34</sup>

## TRITHIOACETALDEHYDE

In the early preparations of thioacetaldehyde an aqueous solution of acetaldehyde was saturated with hydrogen sulfide. An oil was obtained the composition of which was given as  $(C_2H_4S)_n \cdot H_2S$ ,  $n$  having different values up to 8. This showed mercaptan reactions. Treatment of this oil with hydrochloric or sulfuric acid caused crystalline trithioacetaldehyde,  $(CH_3CHS)_3$ , to separate.<sup>54a, 54b, 80, 110a, 110c, 110e, 130, 155, 213</sup> If hydrochloric acid were present when the hydrogen sulfide was passed in, the crystalline compound was formed at once.<sup>12b</sup> Under certain conditions intermediate products having the compositions  $(C_2H_4O)_2(C_2H_4S)$ , m.  $54^\circ$  and  $(C_2H_4O)(C_2H_4S)_2$ , m.  $72^\circ$ , have been obtained. These are believed to have a cyclic structure and to be intermediates between paraldehyde,  $(C_2H_4O)_3$ , and trithioacetaldehyde  $(C_2H_4S)_3$ .<sup>118, 140</sup>

The addition of hydrochloric acid to a solution containing paraldehyde and sodium thiosulfate gives thioacetaldehyde. This is analogous to the preparation of trithiane.<sup>208b, 209a</sup> Hydrogen sulfide and  $\alpha$ -chloroethyl ether give a 70% yield:<sup>112</sup>



It can be prepared by the action of hydrogen sulfide, or a metal sulfide, on  $\alpha, \alpha'$ -dichloroethyl sulfide,  $(MeCHCl)_2S$ .<sup>128</sup>

The monomeric thioacetaldehyde has been reported twice as an odorous liquid boiling at  $40^\circ$  and polymerizing readily.<sup>130, 156</sup>

Thioacetaldehyde and ethyl mercaptan are formed when a 0.025–5% solution of acetaldehyde in 10 to 85% alcohol is saturated with hydrogen sulfide. After 8 days standing the thioaldehyde is no longer detectable. During rectification of the alcohol the thioaldehyde decomposes into acetaldehyde and hydrogen sulfide, but these recombine.<sup>47</sup>

Thioacetaldehyde is formed by the reaction of  $HSMgBr$  (from  $EtMgBr$  and  $H_2S$ ) on acetaldehyde.<sup>135a</sup>

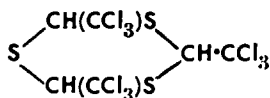
Thioacetaldehyde has been prepared from acetylene by passing it and hydrogen sulfide into 63% sulfuric acid containing mercuric sulfate at  $30$ – $40^\circ$ . Some monothioparaldehyde,  $(CH_3CHO)_2CH_3CHS$ , was isolated, indicating that acetaldehyde was formed first and then converted to the thioaldehyde.<sup>140</sup> Liquid hydrogen sulfide and acetylene combine to a small ex-

tent.<sup>81</sup> Thioacetaldehyde may be made by bringing these two reactants together in the presence of a solvent, such as water or dioxane, under 10 to 20 atmospheres pressure. A catalyst such as potassium hydrosulfide may be added.<sup>93, 94</sup> Trimeric thioacetaldehyde has been prepared by saturating butyl-vinyl ether with hydrogen chloride and then with hydrogen sulfide at  $-10^{\circ}$ .<sup>157, 190</sup>

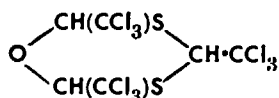
Chloral and hydrogen sulfide form an addition product: <sup>84, 134, 149, 223</sup>



When this is dissolved in conc. sulfuric acid and the solution kept 24 hours at room temperature two compounds are obtained one in  $\alpha$ - and  $\beta$ -forms.

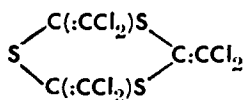


I m.  $181^{\circ}$

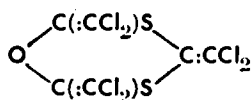


II  $\alpha$  m.  $236^{\circ}$   $\beta$  m.  $108^{\circ}$

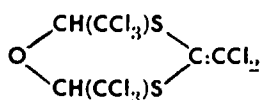
These are dehydrochlorinated by sodium ethylate to IV and V. Sodium acetate removes only one HCl from II, giving VI.



IV m.  $126^{\circ}$

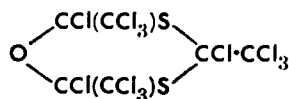
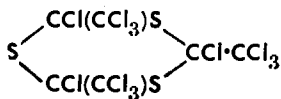


V m.  $89^{\circ}$



VI

Chlorination of these gives the perchlor compounds.



Oxidation of II does not give a stable sulfone but oxidation of VI with hydrogen peroxide yields a mono-sulfone m.  $167^{\circ}$ . The chemistry of this group is complicated.<sup>45</sup>

#### HIGHER THIOALDEHYDES

An unpleasant smelling oil was obtained from *i*-butyraldehyde and hydrogen sulfide but was not characterized.<sup>54a, 54b, 153</sup> The same can be said of propionaldehyde.<sup>54a, 54b</sup> *i*-Valderaldehyde and hydrogen sulfide gave a thioaldehyde  $\text{C}_4\text{H}_9\text{CHS}$ , m.  $69^{\circ}$ , which was considered to be monomolecular in spite of the fact

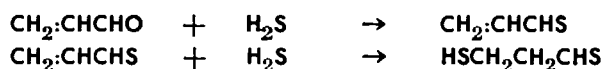
that it was a solid.<sup>188</sup> This preparation was repeated later but no further information was given. Thio-*i*-valeraldehyde, b. 114–5°, has been reported from *i*-valeraldehyde and  $\text{HSMgBr}$ .<sup>110e</sup> Heating *i*-valeraldehyde with sulfur to 250° gave a sulfur containing liquid supposed to be the thioaldehyde boiling at 114–5° along with *i*-valeric acid.<sup>9, 10</sup> In each case the supposed thioaldehyde was probably the mercaptan. A product melting at 94.5° having the composition,  $\text{C}_5\text{H}_6\text{S}_3$ , called trithiovaleraldehyde, was isolated.<sup>9, 10</sup> As has been stated in chapter 1 on Cyclic Sulfides, this has been identified as a trithione.

Hydrogen selenide and *i*-valeraldehyde gave a compound, m. 56.5°, considered to be  $\text{C}_4\text{H}_9\text{CHSe}$ .<sup>118</sup>

The action of ammonium hydrosulfide on dichloroacetic acid gives rise to an acid,  $\text{C}_2\text{H}_2\text{SO}_2 \cdot \text{H}_2\text{O}$ , m. 88–9°, lead salt,  $(\text{CHSCO}_2)_2\text{Pb}$ . The free acid is volatile and unstable. Its high melting point suggests that it is a trimer.<sup>27</sup> The lead salt and ethyl ester, b<sub>3.6</sub> 61°, of this acid have been similarly prepared and desulfurized to  $\text{OCHCOOH}$  indicating the formula,  $\text{SCHCOOH}$ , or a polymer of this.<sup>36</sup> Anthraquinonylglycines have been prepared by the reaction of this acid on reduced aminoanthraquinones.<sup>57</sup>

#### UNSATURATED THIOALDEHYDES

Acrolein reacts with one or with two molecules of hydrogen sulfide:



Thioacrolein,  $\text{CH}_2\text{:CHCHS}$ , is made by heating glycerol with sulfur at 175–200° under 20 lbs. pressure. Unsaturated aldehydes are transformed into unsaturated thioaldehydes by treating them with hydrogen sulfide in a neutral medium.<sup>51, 147, 152</sup> Thioacrolein is said to be germicidal, non-poisonous and suitable for therapeutic uses.<sup>147</sup>

#### ARYL THIOALDEHYDES

These have been synthesized in considerable number and variety. The method that has been used in most cases is to saturate an alcoholic solution of the aldehyde, containing more

or less hydrochloric acid, with hydrogen sulfide. Usually three products are obtained:  $\alpha$ - and  $\beta$ -forms of the cyclic trimer and a mixture of linear polymers. The monomers, which must be formed transiently, trimerize or polymerize instantly. High acidity and high temperature favor the formation of the  $\beta$ -isomer which is believed to be the cis-trans form and is the more stable. If the acidity is lowered so as to obtain more of the  $\alpha$ -form, which is considered to be the cis isomer, linear polymerization is apt to take place. The  $\alpha$ - and  $\beta$ -isomers are usually separated by crystallization from suitable solvents. When there is no evidence to the contrary, the less soluble, more stable isomer, is assumed to be the  $\beta$ -, or cis-trans, form.

By adding ammonium sulfide to an alcoholic solution of benzaldehyde, Laurent in 1841 obtained a mixture from which a compound, melting at 90–95° and having the composition  $C_7H_6S$  was isolated.<sup>117</sup> What may have been the same compound was prepared using potassium pentasulfide.<sup>165</sup> Fifty years later it was characterized as a linear polymer of thiobenzaldehyde. The formula assigned to it was  $(C_6H_5CHS)_{10}$ ,<sup>13a, 13b, 13c</sup> but according to present knowledge of polymers this is to be understood as meaning a mixture having that average composition. By passing hydrogen sulfide into an alcoholic solution of nitrated benzaldehyde a polymeric thionitrobenzaldehyde was obtained as an amorphous, insoluble powder.<sup>24</sup> This was prepared later by another method.<sup>137b</sup> Phosphorus pentasulfide converts aromatic aldehydes and ketones to the thio-.<sup>26</sup>

Of the two cyclic trithiobenzaldehydes, the  $\beta$ -form, melting at 226°, was the first to be isolated.<sup>110a, 110d</sup> Further experiments led to the isolation of the  $\alpha$ -form, m. 167°.<sup>12b, 13b</sup> The two isomers have been studied and reaction conditions found under which either of them can be prepared in high yield. They are separated by crystallization. The  $\alpha$ -isomer is 55 times as soluble in chloroform and 435 times as soluble in benzene at 25° as the  $\beta$ -isomer. The  $\alpha$ -isomer can be converted into the more stable  $\beta$ -form by heating with an acid catalyst.<sup>205</sup> If the reaction is carried out in a low concentration of acid, gummy linear polymers of thiobenzaldehyde result. In alkaline solution benzyl mercaptan and dithiobenzoic acid are by-products. These may be supposed to result from the Cannizzaro reaction of the nascent thiobenz-



aldehyde.<sup>221a</sup> The accepted method of preparation is to pass hydrogen sulfide into an alcoholic solution of benzaldehyde saturated with hydrogen chloride.<sup>112, 221a</sup>

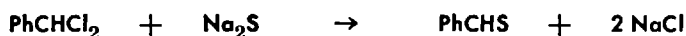
A comprehensive study has been made of the preparation of the  $\alpha$ - and  $\beta$ -isomers of a number of substituted trithiobenzaldehydes. The results showed that the two forms can be obtained only when the substituent is positive or neutral. When a negative substituent is present the lower melting, more soluble  $\alpha$ -isomer can not be obtained. This is true of the hydroxybenzaldehydes unless the phenolic group is alkylated.<sup>218</sup> Linear polymers are apt to form when negative groups are present. A large number of preparations have been made.<sup>13d, 95, 113b</sup> The two forms of 2,4,6-tribenzyl-s-trithiane have been prepared,  $\alpha$ - m. 123°,  $\beta$ -169°. <sup>53</sup> Recently both forms of each of the nine chloro-, bromo-, and iodo-benzaldehydes have been isolated.<sup>197</sup>

From aldehydes derived from polynuclear aromatics such as naphthalene, anthracene and phenanthrene linearly polymeric thials are produced rather than the cyclic trimers. The idea back of the choice of these aldehydes for study was that their large aryl groups might prevent polymerization so that monomeric thials might be isolated. As first obtained the 2-ethoxy-1-thionaphthaldehyde appeared to be monomeric.<sup>220, 221b</sup>

Mesityl aldehyde (2,4,6-trimethyl benzaldehyde)<sup>69</sup> and 9-phenanthrene aldehyde<sup>22</sup> gave only the  $\beta$ -trithials but anisaldehyde,<sup>13c, 13e</sup> furfural,<sup>13c, 13e, 38a</sup> and 2-thiophenealdehyde<sup>203</sup> give both isomers. Thiofurfural has been obtained by sealing up furfural and liquid hydrogen sulfide in a tube and letting this stand at room temperature.<sup>28, 132</sup>

What appeared to be a polymeric thial resulted from passing hydrogen sulfide into an alcoholic solution of 2-ethyl-4-methoxybenzaldehyde containing a trace of piperidine.<sup>122</sup> Thiobenzaldehyde and stilbene were obtained by heating benzaldehyde with sulfur.<sup>10</sup> Thiocinnamic aldehyde is one of the products when allylbenzene is heated with sulfur.<sup>210</sup>

The reaction of benzal chloride with a metal sulfide looks like a plausible way to prepare thiobenzaldehyde:



Several early investigators tried this reaction and got what must have been thiobenzaldehyde polymers.<sup>16, 38b, 63</sup> This method has

been used recently.<sup>221a</sup> When an excess of potassium sulfide was used benzyl disulfide and dithiobenzoic acid were isolated indicating that thiobenzaldehyde had been formed but had undergone the Cannizzaro reaction.<sup>110d</sup>

A thioaldehyde may be an intermediate in the Willgerodt reaction.<sup>108a</sup>

## Thioketones

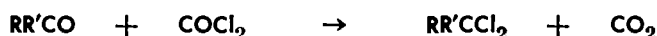
### ALIPHATIC THIONES

The regulation method of preparing a thioketone is to saturate the ketone, or a solution of it, with hydrogen chloride and hydrogen sulfide. Acetone,<sup>65, 112</sup> methyl ethyl ketone,<sup>35, 119</sup> cyclohexanone,<sup>64c, 158b, 189a, 189c, 189d</sup> cyclopentanone,<sup>64c, 189a, 189c, 189d</sup> pulegone,<sup>64c</sup> camphor,<sup>158b, 189a, 189c, 189d</sup> fenchone,<sup>189a, 189c, 189d</sup> benzophenone,<sup>200a</sup> and other ketones<sup>30</sup> have been converted to thioketones in this way. The thioketones from acetone,<sup>65</sup> methyl ethyl ketone,<sup>119</sup> cyclopentanone,<sup>64c</sup> 1-indanone, 1-tetralone, 3-Me-tetralone,<sup>41</sup> and pulegone<sup>64c</sup> were found to be trimeric, the ones from camphor, mono-, di- or tri-meric, from cyclohexanone, mono-<sup>158b</sup> or trimeric,<sup>64c, 189a, 189c, 189d</sup> from fluorenone, mono-<sup>42</sup> or dimeric,<sup>19, 42</sup> from 3-Me-1-indanone, mono- or trimeric,<sup>41</sup> and the ones from benzophenone<sup>30, 200a</sup> and 3-Ph-1-indanone monomeric only. Acetylacetone, hydrogen sulfide, and hydrogen chloride give a mixture of two isomeric dithioketones of the composition,  $C_{10}H_{16}O_2S_2$ . Tricyclic structures have been proposed for these.<sup>33</sup> Treating chloroacetone with hydrogen chloride and hydrogen sulfide gives a compound which was supposed to be the dithioketosulfide,  $(MeCSCH_2)_2S$ ,<sup>35</sup> but which has been shown to be 2,6-dimethyl-(2,6-endo-sulfido)-1,4-dithiane.<sup>25</sup> Thioketones suitable for use as fungicides and insecticides are produced from ketones and hydrogen sulfide in the presence of a dehydration catalyst.<sup>215</sup>

The thioketones obtained by treating ketones with hydrogen sulfide and hydrochloric acid are frequently impure owing to incompleteness in the replacement of oxygen by sulfur. A method which gives exceptionally pure products is the treatment of a ketone chloride with thioacetic acid: <sup>109, 141, 185, 196a</sup>



The ketone chloride may be prepared from the ketone and phosgene: <sup>109</sup>

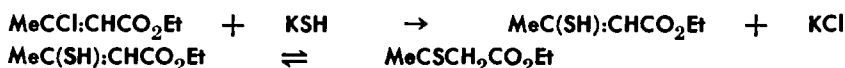


The chloride from benzophenone reacts with alkali sulfide or hydrosulfide to give a good yield of thiobenzophenone: <sup>15, 56a, 71, 200a, 200c</sup>



The thioketone,  $Me_2CHCSCO_2H$ , results from the treatment of isopropylidene-rhodanine with sodium hydroxide.<sup>125</sup>

Refluxing ethyl  $\beta$ -chlorocrotonate with potassium hydrosulfide gives thioacetoacetic ester: <sup>62, 137c, 158a</sup>



This is an orange colored liquid,  $b_{15} 75^\circ$ ,  $d_{31/4} 1.0554$ ,  $n_{26/D} 1.4712$ .<sup>137a, 137b, 137c</sup> It can be alkylated and evolves hydrogen sulfide with phenylhydrazine and hydroxylamine. A much better yield is obtained by passing hydrogen sulfide into an alcoholic solution of acetoacetic ester saturated with hydrogen chloride. Its dipole moment has been measured in several solvents.<sup>62</sup> Analogous thioketo esters can be made from alkyl acetoacetic esters and from acetylmalonate ester. These exist partly in the "enol" form,  $MeC(SH):CHCO_2Et$ , the proportion of which is greater in the substituted esters.<sup>137a, 137b, 137c, 158a, 159</sup>

The interesting thing about thioacetoacetic ester is that it reacts with aldehydes to give high yields of thioaldehydes.<sup>158a</sup> Trithioformaldehyde, trithiobenzaldehyde, trithioanisaldehyde and trithiovanilline have been prepared in this way.<sup>137a, 137b, 137c</sup>

From ethyl  $\beta$ -chloro-isocrotonate a stereoisomeric ester,  $MeC(SH):CHCO_2Et$ ,  $b_{18} 77^\circ$ ,  $d_{29.5/4} 1.0747$ , has been prepared.<sup>166, 167</sup>

A different method is the treatment of a ketone with ammonium sulfide. Acetone gave a product melting at  $98^\circ$  and boiling at  $243^\circ$ ,<sup>214</sup> compared with  $24^\circ$  and  $225-30^\circ$ , for that obtained in the presence of hydrochloric acid. By heating camphor with ammonium sulfide, mixtures have been obtained from which thio-camphor has been isolated.<sup>168, 222</sup> Benzylidene-acetone, with ammonia and hydrogen sulfide, gives a mixture which has been

difficult to handle. Its chief constituent has been found to be duplobenzylidenedithioacetoneamine.<sup>64a, 64b, 66, 67b</sup>

Magnesium bromohydrosulfide,  $\text{BrMgSH}$ , can be used to convert acetone into trithioacetone: <sup>135b</sup>



Thioketones appear to be intermediates in the Willgerodt reaction.<sup>43, 108b</sup>

Acetone ethyl mercaptole breaks down into thioacetone and ethyl sulfide.<sup>12a</sup>

By heating acetone with phosphorus pentasulfide a product, boiling at  $183-5^\circ$ , has been obtained. This has been called "duplo-sulfacetone" since its analysis and molecular weight correspond to the formula,  $(\text{C}_3\text{H}_6\text{S})_2$ .<sup>216</sup> As it is believed to have a cyclic structure, it has been considered under cyclic sulfides in chapter 1. A number of thioketones have been prepared similarly. Those from dimethyl, methylethyl, and diethyl ketones are dimers, the one from dipropyl a mixture of monomer and dimer, and the one from di-*t*-butyl, a monomer.<sup>115</sup>

Dimethyl pyrrondicarboxylate, heated with phosphorus pentasulfide, is transformed into the corresponding thio-compound.<sup>83</sup> Pyridone<sup>161</sup> and piperidone<sup>114, 161</sup> give similar results. Thio-menthone,  $\text{C}_{10}\text{H}_{18}\text{S}$ , b.  $217-20^\circ$ ,  $d_{15}$  0.9398, was prepared by heating menthone with phosphorus trisulfide. Camphor, methylhexanone,<sup>195</sup> caffeine, and theobromine<sup>107</sup> react similarly.

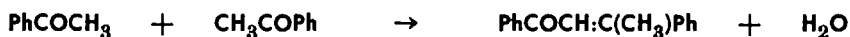
Thioketones, suitable for sensitizing photographic silver halides, are said to be produced by heating a vinyl halide with a metal sulfide.<sup>111</sup>

#### ALKYL ARYL THIONES

The only member of this group that has received much attention is thioacetophenone, which is of special interest since it can be obtained in both the monomeric and trimeric forms.

When hydrogen sulfide reacts with acetophenone, in alcohol in the presence of hydrogen chloride, four products can be obtained: monomeric thioacetophenone, its trimer, anhydrotri-acetophenone, and a green resin. In the usual preparation the solution takes on an intense blue-violet color, indicating the presence of the monomer. On standing, the solution loses its color, and white crystals of the trimer are deposited. The anhy-

drothioacetophenone has the composition,  $C_{24}H_{22}S_2$ , which differs from that of trithioacetophenone,  $C_{24}H_{24}S_3$  by one molecule of hydrogen sulfide.<sup>12c</sup> The reaction can be so conducted that the anhydrothioacetophenone is the chief product.<sup>39a</sup> It is well known that two molecules of acetophenone condense to dyprone:



It seems likely that the compound in question is formed by the addition of monomeric thioacetophenone to thiodyprone.

Trithioacetophenone crystallizes from alcohol in needles which melt at  $122^\circ$  to a colorless liquid. On further heating it turns green, then deep blue, and at about  $185^\circ$  gives off hydrogen sulfide and a bluish-violet vapor. There should be two isomeric forms, but only one is known. It has not been oxidised to a sulfone. This vapor can be condensed to a blue liquid which is probably the monomer. It can not be purified on account of its instability. On distillation it gives a number of products: styrene, ethylbenzene, 2,4-diphenylthiophene, and sulfur. Under the influence of acids it trimerizes. Boiling with water converts it to acetophenone.<sup>12c, 53</sup> 2-Acetylthiophene give 2-thienyl-methylthione, a violet oil, which appears to be the monomer.<sup>203</sup>

Magnesium bromohydrosulfide converts acetophenone into the thione.<sup>135b</sup> Heating ethyl cinnamate with sulfur produces a compound which, when pyrolyzed, gives thioacetophenone and 2,3-diphenylthiophene.<sup>12d</sup> From acetophenone and ammonium sulfhydrate a compound was obtained which was thought to be a thioketone<sup>56b, 126</sup> but was finally shown to be 2,3-diphenylthiophene.<sup>67a</sup> The possible presence of thioketo groups in vulcanized rubber has been studied.<sup>85, 97, 98, 101, 148</sup>

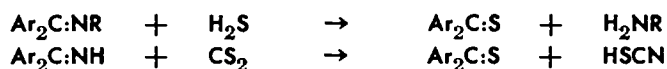
### ARYL THIONES

Thiobenzophenone was first prepared by saturating a cold alcoholic solution of benzophenone with hydrogen chloride and hydrogen sulfide. It was obtained as deep blue needles, melting at  $52^\circ$ . It is sensitive to air oxidation and must be handled in an atmosphere of carbon dioxide.<sup>200a</sup> Various reagents reconvert it to benzophenone.<sup>99</sup> In an attempt to prepare phenyl-2-thienylthione, in the same way, a green oil was obtained which was not characterized.<sup>203</sup> Phenyl-diphenylthione, phenyl- $\alpha$ -naphthylthi-

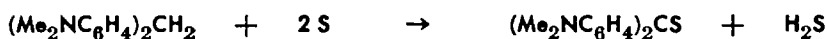
one and phenyl-*p*-tolylthione have been made by this method. They are stable monomers.<sup>30</sup>

Benzophenone is obtained readily from benzene and phosgene by the Friedel and Crafts reaction. This does not go so well with thiophosgene, but some thiobenzophenone seems to have been obtained in this way.<sup>23</sup> However, alkoxy- and dialkylamino-benzenes are readily converted to the corresponding substituted thiobenzophenones by this means.<sup>70, 108, 177</sup>

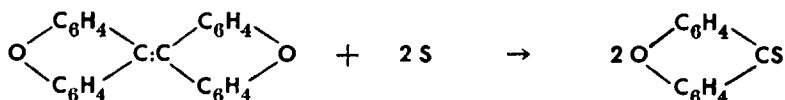
Some ketone-imides can be split by hydrogen sulfide<sup>59, 77b, 78, 124, 160</sup> or by carbon disulfide:



Auramine is converted to the thioketone,  $(\text{Me}_2\text{NC}_6\text{H}_4)_2\text{CS}$ , by hydrogen sulfide.<sup>59, 77a, 207</sup> 4-Chloroquinoline-methiodide and sodium sulfhydrylate give 1-methyl-4(1 H)-quinolinethione.<sup>40</sup> In a few cases sulfur changes a methylene group to a thiocarbonyl: 7b, 55, 138, 212



Acridine takes up sulfur at 200° to form thioacridone.<sup>96</sup> Dixanthylene seems to be the only stilbene derivative that can be sulfurized directly to the thioketone:<sup>177</sup>



Certain methylene compounds are said to be converted to dithioketones by sulfur monochloride:<sup>142, 143, 144</sup>



The structural formulae given for the products require confirmation. Phenyl benzyl ketone is converted to a trimeric thioketone by thiophosgene,  $\text{SCCl}_2$ .<sup>133</sup>

Michler's ketone can be transformed into the corresponding thioketone by heating with phosphorus pentasulfide.<sup>7a</sup>

Thioketones are produced by the thermal decomposition of certain sulfides, disulfides, and thioketals. A sort of disproportionation takes place with dixanthyl sulfide in boiling benzene:<sup>182</sup>



Bornyl disulfide gives thiocamphor and bornyl mercaptan: <sup>89, 164, 222</sup>



Dibenzhydryl disulfide breaks down into thiobenzophenone and diphenylmethane with loss of sulfur: <sup>222</sup>

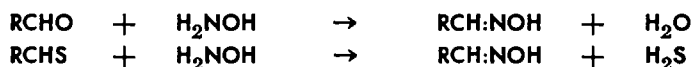


Benzyl mercaptols of aromatic ketones are thermally unstable. They give thioketones and decomposition products of benzyl sulfide. <sup>180, 181</sup>

### Reactions of Thials and Thiones

#### GENERAL

With reagents such as hydroxylamine and phenylhydrazine, which remove the carbonyl oxygen from aldehydes and ketones, the reactions of thials and thiones are similar:



They are easier to follow since the hydrogen sulfide that is given off is a measure of their progress. <sup>8, 24, 78, 116, 160, 193, 222</sup> The reaction of vulcanized rubber with hydrazine has been attributed to the presence of thioketone groups. <sup>97, 102</sup>

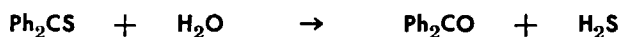
#### OXIDATION

Thiobenzophenone, unlike other diaryl thioketones, is easily oxidised by air even at room temperature. The chief product is benzophenone <sup>15, 71, 175</sup> but there is a curious by-product,  $\text{Ph}_2\text{C}:\text{S}_3:\text{CPh}_2$ , a trisulfide to which different formulae have been assigned. Sulfur and sulfur dioxide are also formed. <sup>71, 184, 185, 200a, 200b</sup> The oxidation is catalyzed by light. This conversion of a thioketone to a ketone by oxidising agents must be connected with the ability of bivalent sulfur to take up oxygen. <sup>208</sup> Triethylphosphine aids the oxidation. <sup>174</sup> In contrast to this, *p*-dianisylthioketone is unaffected when air is bubbled through its boiling toluene solution. <sup>174</sup> This thione and dimethylaminobenzothione are stable to oxygen in the dark but not in sunlight, while *N*-phenylthioacridone, 4-thioflavone, and 2,6-diphenylthiopyrone are stable even in sunlight. <sup>175</sup>

Dimethoxythiobenzophenone,  $(\text{MeOC}_6\text{H}_4)_2\text{CS}$ , is converted to the oxygen compound by hydrogen peroxide.<sup>109</sup> The same is true of thiobenzophenone. The sulfur goes to the sulfate ion.<sup>100, 102, 103</sup>

### HYDROLYSIS

Thioketones are hydrolyzed to ketones by water either in the absence<sup>44</sup> or presence of acids or bases.<sup>99, 137a</sup> Some benzophenone is formed when thiobenzophenone is heated with water:<sup>70</sup>



This reaction is aided by dilute nitric,<sup>110b</sup> hydrochloric,<sup>8</sup> or sulfuric acid.<sup>212</sup> Alkali may lead to the same result:<sup>71</sup>



Diphenylthioketene is unstable and polymerizes immediately. The polymer probably has the structure,  $[\text{C}(:\text{CPh}_2)\text{S}]_n$ .<sup>201</sup>

### DESULFURIZATION

Thials and thiones lose sulfur, when heated, forming ethylene derivatives:<sup>127, 137b</sup>



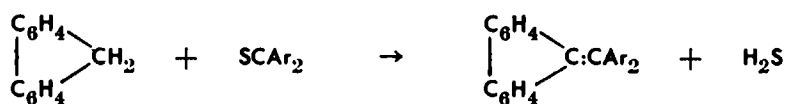
The dry distillation of thiobenzaldehyde gives stilbene, a part of which is converted to tetraphenylthiophene by the sulfur.<sup>13e, 14, 15, 63, 88, 200a, 221a</sup> A number of trimeric aromatic thials have been converted to stilbenes by heating. In the case of *o*-methoxythiobenzaldehyde the conversion to tetra-*o*-methoxyphenylthiophene is complete at 145°. <sup>113a, 113b</sup> A large variety of heterocyclic thiones have been studied. There are wide differences in their stabilities.<sup>2, 3, 4, 171, 175</sup> Sulfur is eliminated similarly from the diaryl thiones. Thiobenzophenone gives off its sulfur at 170° leaving tetraphenylethylene: <sup>15, 200a</sup>



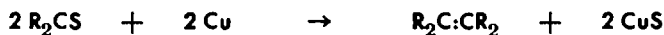
Some derivatives of 4-thiopyrone lose the sulfur on standing at room temperature.<sup>4</sup>

In a few cases the sulfur of a thioketone may be removed by the hydrogen of an activated methylene group such as is found in fluorene<sup>177</sup> or in xanthene:<sup>182</sup>

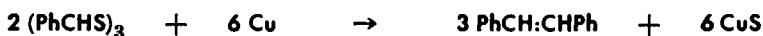




While the sulfur can be driven off, it is better to take it off by some metal that combines with it readily:



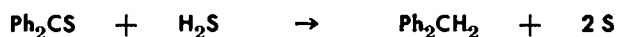
Activated copper is the metal commonly used; but iron, zinc, and nickel have been found to be effective.<sup>10, 22, 69, 70, 71, 110a, 122, 141, 163, 173, 203, 216, 220</sup> Even cyclic trimers undergo this reaction. Trithiobenzaldehyde is converted to stilbene: <sup>10, 110a, 220</sup>



Trithioacetone,<sup>216</sup> trithiovanilline,<sup>000</sup> trithioveratraldehyde,<sup>163</sup> trithiomesitaldehyde,<sup>69</sup> and trithiothiophene aldehyde<sup>203</sup> are converted to the corresponding stilbene derivatives by heating with copper powder. With the aromatic thioketones, where there are two aryl groups on one carbon atom and no cyclization, the removal of sulfur is even simpler. Boiling a xylene solution of a thioketone with copper powder is a recognized method of preparing substituted stilbenes.<sup>70, 71, 173</sup> By treating certain thiopiperidones with a metal oxide and ammonia the sulfur atom is replaced by the imino group.<sup>72</sup>

### REDUCTION OF THIONES

By the Clemmensen method phenylthiopyruvic acid is completely desulfurized.<sup>79</sup> Thioborneol is reduced to bornyl mercaptan.<sup>189a, 189b</sup> Xanthione is reduced to 9,9'-dixanthyl.<sup>182</sup> *p,p'*-Tetramethyldiaminodiphenylmethane is obtained from the thioketone.<sup>8</sup> By sodium amalgam, phenylthiopyruvic acid is converted to the mercapto-acid<sup>79</sup> and dithioacetone to *i*-propyl mercaptan.<sup>196b</sup> Thiofenchone is reduced by aluminum amalgam in ether to fenchyl mercaptan.<sup>164, 189a</sup> Curiously enough, hydrogen sulfide may remove the sulfur from thiobenzophenone: <sup>160</sup>



The same thione is reduced by ammonium sulfide to the disulfide,  $\text{Ph}_2\text{CHS}\cdot\text{SCHPh}_2$ . This is true of other diaryl thiones.<sup>20</sup> Hydrogenation with Raney nickel converts trithioacetophenone to symmetrical dimethyldiphenyl stilbene.<sup>48</sup> Thioketones are reduced by

Raney nickel to the hydrocarbons.<sup>32</sup> Hydrogenation gives the mercaptan: <sup>58</sup>



Hydrogenation of thiobenzophenone over a ruthenium catalyst gives much dibenzyl and some stilbene.<sup>49</sup>

#### OTHER REACTIONS

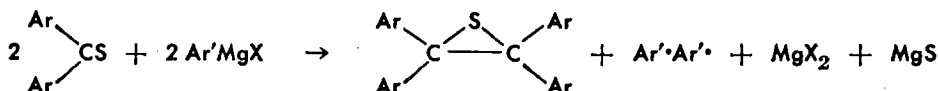
A metalo-organic compound may add to a thioketone as it would to an ordinary ketone: <sup>19, 21</sup>



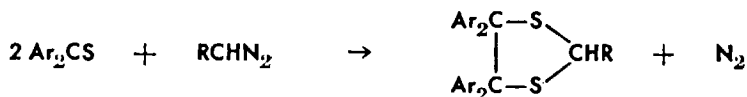
Hydrolysis gives a tertiary mercaptan which may lose hydrogen sulfide: <sup>17, 19</sup>



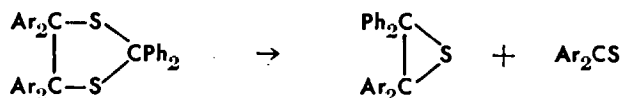
Tetra-arylethylene sulfides may result from the reaction of a Grignard reagent on a diaryl thioketone:



In some cases the sulfur is thrown out, leaving a tetra-arylethylene,  $\text{Ar}_2\text{C:CAr}_2$ .<sup>177, 178</sup> The same products can be gotten with magnesium iodide and magnesium.<sup>183</sup> A similar tetraphenylethylene sulfide, which loses sulfur in the same way, results from the reaction of thiobenzophenone with diphenyldiazomethane.<sup>202</sup> Diaryl thiones react with diazomethane, diazoethane, or diazoacetic ester, to give a cyclic thial with two sulfur atoms in the ring: <sup>20, 131, 172</sup>



This ring may contract to the ethylene sulfide ring with the elimination of a molecule of the aryl thione: <sup>176</sup>



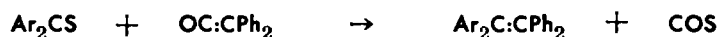
It seems possible that the usual sequence of events is the formation of the five membered ring, the transformation of this into

the three membered ethylene sulfide ring, and the elimination of sulfur to give the stilbene as the final product.

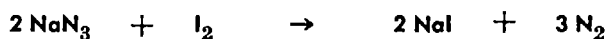
The sulfur is eliminated when a diaryl thione is treated with phenylazide<sup>187</sup> or isocyanate:<sup>199</sup>



The reaction with diphenyl ketene looks to be similar but is supposed to go through a cyclic intermediate:<sup>198, 200a</sup>



The  $>\text{C:S}$  group is detected and estimated by its influence on the reaction of sodium azide and iodine:<sup>60, 61</sup>



In this it is less efficient than the mercaptan group but more so than the disulfide.<sup>6</sup>

#### COMPLEXES WITH METAL SALTS

The addition compounds of trithioformaldehyde and trithioacetaldehyde have been considered briefly in the chapter on cyclic sulfides.

The monomolecular thiones form colored complexes with a wide variety of heavy metal salts. The ratio of thione to metal may vary with the method of preparation. It is curious that two or even three molecules of a thione may unite with a single molecule of a metal salt. There are color shifts when these complexes are formed. In spite of the amount of study that has been put on these complexes their constitution is not yet clear.<sup>2, 145, 154, 177, 186, 192</sup> Thio-Michler's ketone is an analytical reagent for certain heavy metals.<sup>74</sup> Isonitrosothiocamphor is a sensitive reagent for cobalt.<sup>189b</sup>

#### Structure of Thioketones

The dipole moments of several thioketones have been contrasted with those of the corresponding ketones; the value for a thione is about half a unit greater than that for its oxygen counterpart. This is taken to show a structural difference between the  $\text{C:O}$  and  $\text{C:S}$  groups.<sup>18, 52, 90, 191</sup>

There are anomalies in the magnetic rotation dispersion of thiobenzophenone.<sup>50</sup> This thione is diamagnetic with a mass

susceptibility of  $-0.677$ . The magnetic test is not decisive for biradicals.<sup>1</sup>

The bond energy for the  $C=O$  group is 152 kg.-cal. while that for the  $C=S$  group is much less, 103. The single bond  $C-O$  is 70;  $2 \times 70$  is 140 which is less than 152, indicating the stability of the carbonyl group. With sulfur the single bond,  $C-S$ , is 54.5 and  $2 \times 54.5$ , 109, is greater than 103. This is in accordance with the tendency of thioaldehydes and aliphatic thioketones to trimerize by which carbon-sulfur double bonds are converted to single. The interatomic distances, 1.61 Å for  $C=S$  and 1.26 for  $C=O$  are in accordance with the bond strengths.<sup>150, 151</sup> The refractivity of the sulfur is 9.70.<sup>31</sup> Trithioacetone has been considered an equilibrium mixture of three structural forms.<sup>104</sup>

Practically all of the monomeric thiones are colored. The development of color in the trimer is taken to indicate its dissociation into a monomer. Thus the color of a xylene solution of trithioacetophenone deepens on heating and becomes pale on cooling. Similar color changes have been noted for other thiones.<sup>46, 146</sup> It is a curious fact that the introduction of an auxochrome group may lighten, rather than deepen, the color of thiobenzophenone. This indicates that the origin of the color in thiobenzophenone is different from what it is in malachite green.<sup>18, 20, 202, 204</sup>

The absorption spectra of a number of thiones have been studied and compared with those of the ketones.<sup>30, 37, 52, 120b, 123, 189a</sup> The absorption band is shifted toward the red by the sulfur.<sup>37</sup> The long wave length absorptions of the thiones have been tabulated and compared to those of their oxygen analogs.<sup>123</sup> The ultraviolet curves of the sulfur and oxygen compounds are decidedly different, indicating different structures for the  $C=O$  and  $C=S$  groups.<sup>52</sup> The color characteristics of aryl thiones suggest a kinship with the triarylmethyls and indicate the presence of free radicals.<sup>20</sup>

The phosphorescence of thiobenzophenone has been attributed to its triplet, or biradical state. The abnormal colors of the monomeric thiones appear to be due to the absorption from the singlet to the triplet state.<sup>105, 120a, 120b</sup>

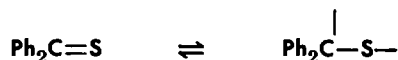
### Thioketones and Free Radicals

Schönberg<sup>170b</sup> has called attention to the many analogies between thioketones and triarylmethyl compounds. The substitu-

ents which increase the stability of free radicals have the same effect on thione monomers. The fact that diphenyl disulfide,  $\text{PhS}\cdot\text{SPh}$ , does not obey Beer's law at somewhat elevated temperatures, indicates that it tends to dissociate into free radicals: <sup>179</sup>



In thiobenzophenone the fourth valence of the carbon atom and the second of the sulfur may be considered as weak and represented by a thin valence line. The double bond would tend to become a single bond joining two free radicals, somewhat like Thiele's partial valencies:



The equilibrium between these two would be determined by the nature and size of the two radicals joined to the carbon atom. The biradical would tend to combine with other biradicals, as in the trimerization of thioketones, which in turn might dissociate. Attention is called to the fact that a free radical does not exist of and by itself. The strength of a bond depends not upon what is at one end, but upon the two groups which it joins. Thus triphenylmethyl chloride is stable but hexaphenylethane, in which one potential free radical is joined to another, is unstable. Diphenyl ketone is stable and colorless, but diphenyl thioketone is colored and tends to dissociate <sup>20</sup> because both ends of the potential biradical tend to become free radicals.

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## CHAPTER 3.

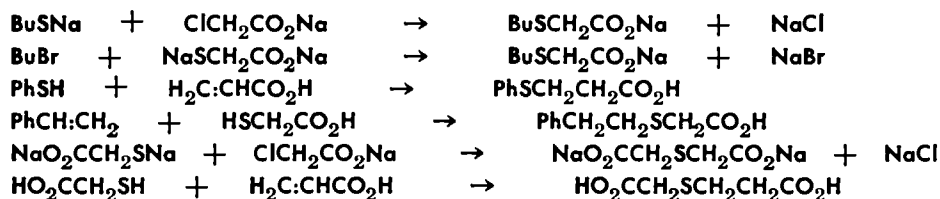
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# Sulfide-Acids

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These are acids such as ethylmercaptoacetic,  $\text{EtSCH}_2\text{CO}_2\text{H}$ , or ethylmercaptobenzoic,  $\text{EtSC}_6\text{H}_4\text{CO}_2\text{H}$ , in which there is a sulfide grouping and also a carboxyl. As neither of these interferes with the reactions of the other, sulfide-acids have the two sets of characteristics. As acids they resemble closely acids of similar structure and molecular weight that do not contain sulfur. A similar statement can be made about them as sulfides.

Sulfide-acids may be synthesized by any of the methods that are appropriate for sulfides. The chief of these are the reaction of an alkyl halide with a mercaptide and the addition of a mercaptan to an unsaturate. In each of these the carboxyl group may be in either the one or the other of the reactants. If both contain carboxyls the product will be a dibasic acid. The following reactions are typical:



Another way to make a sulfide-acid is to introduce a carboxyl into a sulfide by any appropriate method.

The methyl ester of a sulfide-acid,  $\text{MeSCH}_2\text{CH}_2\text{CO}_2\text{Me}$ , has been isolated from pineapples, 1 g. from 1000 kg. of the pulp. Its constitution has been confirmed by synthesis.<sup>177</sup> As will appear



later in this volume, methionine, an important constituent of proteins, is an aminosulfide-acid.

### Syntheses

#### FROM A MERCAPTIDE AND A HALOACID

The simplest sulfide-acids are the alkyl thioglycolic acids,  $\text{RSCH}_2\text{CO}_2\text{H}$ , and their alkyl derivatives,  $\text{RSCHR}'\text{CO}_2\text{H}$  and  $\text{RSCR}'\text{R}''\text{CO}_2\text{H}$ , which are obtained readily by the reaction of a mercaptan with chloracetic acid, or one of its alkyl derivatives, in alkaline solution. The first member of this series,  $\text{CH}_3\text{SCH}_2\text{CO}_2\text{H}$ , was gotten from iodoacetic acid and methyl disulfide but just how is not clear.<sup>280</sup>

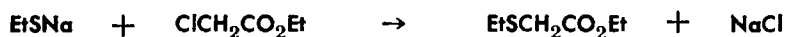
An aqueous solution of the sodium salt of the halogen acid is added to an alkaline solution of the mercaptan. The reaction is rapid, even below room temperature. The mixture may be left overnight or warmed to insure the completion of the reaction. Volatile impurities, such as an excess of the mercaptan, may be removed by steam distillation. The remaining solution is filtered and acidified. Extraction with ether is desirable for acids containing small alkyls. The yields are high. To avoid air-oxidation of the mercaptan, which is rapid in alkaline solution, the mercaptan should be added to the alkali just before the final mixing. Or the halogen acid, the mercaptan, and water may be mixed and the alkali added.<sup>352, 425, 426, 427</sup> Better results are obtained by adding a concentrated aqueous solution of the sodium mercaptide, dropwise with stirring, to a concentrated solution of sodium chloracetate, cooled below  $0^\circ$ . This minimizes the alkaline hydrolysis of the halide acid. After standing overnight the mixture may be heated.<sup>334a, 334b</sup> In the preparation of butyl- and benzyl-thioglycolamides, from the sodium mercaptides in absolute alcohol and chloracetamide, excellent yields were obtained when the mixtures were kept cold, as above, but poor yields when they were heated at once.<sup>117, 424</sup> A number of alkylthioglycolic amides,  $\text{RSCHR}'\text{CONH}_2$ , in which R is ethyl, propyl, and butyl and R' is methyl and ethyl have been made.<sup>334a, 334b</sup> Arylmercaptoacetic acids have been prepared from benzyl mercaptan and from thioresorcinol.<sup>154a</sup>

The halogen acid and the mercaptan may be dissolved in a basic liquid, such as pyridine or piperidine, which serves as a solvent and an acid binding agent.<sup>409</sup>

$\beta$ -Propiolactone reacts with a sodium mercaptide, as if it were a  $\beta$ -halopropionic acid, to give an alkyl- or arylmercaptopropionic acid. A number of aliphatic,<sup>172a</sup> several aromatic,<sup>171, 172a</sup> and thiazolyl mercaptans<sup>166b, 172c, 231</sup> have been used with it. The acid,  $\text{PhNHC}(:\text{NH})\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , has been made from it and thiourea.<sup>172d</sup>  $\gamma$ -Butyrolactone reacts similarly.<sup>15, 254, 332, 416</sup> Other acids of this group have been made from  $\beta$ -chloropropionic acid and methyl,<sup>177</sup> ethyl,<sup>94</sup> phenyl,<sup>143</sup> and *p*-nitrophenyl<sup>35</sup> mercaptans. The ethyl,<sup>112</sup> propyl,<sup>406</sup> butyl,<sup>112</sup> and *p*-bromophenyl<sup>74</sup> acids,  $\text{RSCH}_2\text{CH}_2\text{CO}_2\text{H}$ , have been made from  $\beta$ -bromopropionic acid and the mercaptans. To check these, the ethyl and butyl acids were made from the alkyl halides and  $\beta$ -mercaptopropionic acid.<sup>112</sup> Some other acids are  $\text{PhSCHMeCO}_2\text{H}$ ,<sup>343</sup>  $\text{PhSCMePhCO}_2\text{H}$ ,<sup>49</sup> and  $\text{PhCH}_2\text{SCHEtCO}_2\text{H}$ .<sup>62</sup> The acid,  $m\text{-C}_6\text{H}_4(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , has been made from dithioresorcinol.<sup>138</sup>

A large number of alkyl and aryl mercapto-acetic acids and derivatives have been prepared in a study of the biosynthesis of penicillins. Many of them are utilized by molds to produce a variety of new penicillins.<sup>32, 34, 143, 394</sup> For a study of antiseptic properties acids  $\text{RSCHR}'\text{CO}_2\text{H}$ , in which R was dodecyl, tetradecyl, or cetyl and R' hydrogen or an alkyl, were prepared from the  $\alpha$ -bromoacid and a mercaptide.<sup>196</sup> A series of acids,  $\text{Me}(\text{CH}_2)_n\text{S}(\text{CH}_2)_m\text{CO}_2\text{H}$ , in which *n* varied from 0 to 9 and *m* from 1 to 10 and  $n + m = 10$ , has been reported. Some of these were from the haloacids and mercaptides, some from the halides and mercaptoacids.<sup>345</sup>

Esters of alkylmercaptoacetic acids have been made from alkyl haloacetates and sodium mercaptides in alcohol solution: <sup>91, 246, 250a, 250b, 298, 429, 445</sup>



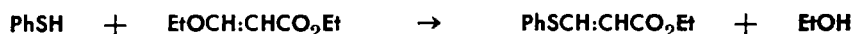
The proper way to carry out this reaction is to dissolve a weighed amount of sodium in absolute alcohol, cool in ice, and add the calculated amount of the mercaptan at once. The formation of the sodium mercaptide is instantaneous on simple mixing. Gradual addition of the mercaptan and heating favor oxidation of the mercaptan by air. The haloester is added at such a rate that the temperature does not rise appreciably. The course of the reaction is observed by the precipitation of sodium halide which usually begins in a few minutes. The reaction mixture is

kept for some hours at room temperature and may then be heated briefly. The sodium halide is filtered off and washed with a little alcohol. The alcoholic solution of the ester is concentrated. To throw out any traces of inorganic salts, the concentrate may be taken up in ether and refiltered, but this is hardly necessary. The concentrate is fractionated. This is suitable for aromatic mercaptans as well as aliphatic.<sup>351</sup>

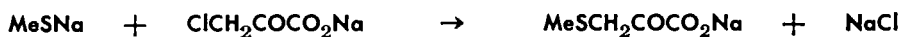
The reaction of sodium thiophenate with sodium bromoacetate is extremely rapid.<sup>197</sup> Many sulfide-acids have been made from substituted thiophenols and chloracetic acid.<sup>91, 121, 152, 155, 194, 216, 220, 417</sup> Mercaptoanthraquinones,<sup>285</sup> a mercaptoanthracene,<sup>151</sup> a mercaptodiphenyl,<sup>21</sup> a mercaptopyrimidine,<sup>69, 89, 200</sup> a mercaptobenzothiazole,<sup>120</sup> and a mercaptoimidazole<sup>156</sup> have been used in making other sulfide-acids.

In alkaline solution thiophenethiol-2 has been caused to react with ethyl chloracetate<sup>73, 81</sup> and thiophenethiol-3 with chloracetic acid.<sup>59, 81</sup>

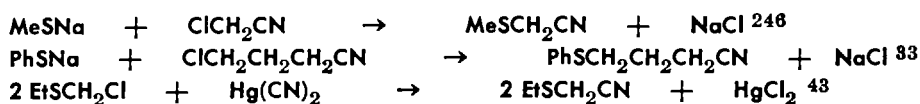
A sulfide-acid has been prepared from 2-chloro-5-nitrobenzoic acid and *p*-chlorothiophenol.<sup>264</sup> 4-Alkylmercapto-3-nitrobenzoic acids have been made starting with 3,4-nitrochlorobenzoic acid. These can be reduced to the corresponding aminoacids.<sup>115</sup> The diazonium chloride, *o*-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>Cl, and thiophenol give the acid, *o*-PhSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H.<sup>435</sup> In some cases an alkoxy group can be replaced: <sup>97, 98</sup>



Ketosulfide-acids have been made: <sup>134, 329, 330</sup>

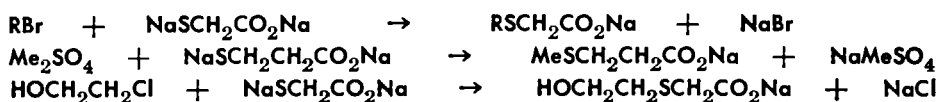


Frequently sulfide-acids are made by way of the nitriles which are subsequently hydrolyzed: <sup>24, 50, 75, 203</sup>



#### FROM AN ALKYL HALIDE AND A MERCAPTO-ACID

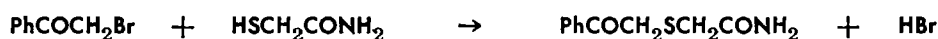
Sulfide-acids can be made, the other way around, by the reaction of an alkyl halide or sulfate with a mercapto acid in alkaline solution: <sup>12, 20, 126, 142, 143, 184b, 192, 206b, 209d, 271a, 273b, 277, 388</sup>



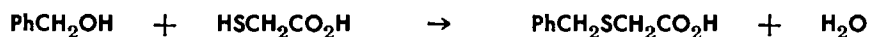
The acids,  $\text{MeSCHMeCO}_2\text{H}$  <sup>297b</sup> and  $\text{AmSCH}_2\text{CO}_2\text{H}$ , <sup>234</sup> have been prepared in this way. The acid,  $\text{DL-MeCHPhSCH}_2\text{CO}_2\text{H}$ , has been resolved. <sup>207a</sup> Several alkylthiocrotonic acids have been prepared. <sup>9, 80, 369, 370</sup> There has been much interest in determining their configurations. <sup>301</sup> Nitrophenyl sulfide-acids have been made from nitrophenyl chlorides and thioglycolic acid. <sup>139, 221, 242</sup> The anilide of thioglycolic acid and the toluide of  $\alpha$ -mercaptobutyric acid react well with alkyl halides. <sup>28b, 28d</sup> 2,4-Dinitro- $\alpha$ -naphthylmercaptoacetic acid has been prepared. Its chloride can be condensed to the 1,8-thiolactone. <sup>278</sup> In the presence of sodium carbonate, diphenyl iodonium chloride reacts with thioglycolic acid to give phenyl iodide and phenylmercaptoacetic acid. <sup>365</sup> A number of alkylmercaptosuccinic acids,  $\text{HO}_2\text{CCH}(\text{SR})\text{CH}_2\text{CO}_2\text{H}$ , have been prepared from mercaptosuccinic acid and alkyl halides. <sup>25, 140a</sup> Alkylmercaptocrotonic acid esters can be made from the sodium salt of the thioacetoacetic ester,  $\text{MeC}(\text{SNa})\text{:CMeCO}_2\text{Et}$ , and an alkyl sulfate. <sup>303b</sup>

Aromatic sulfide-acids have been made from mercaptobenzoic acids and alkyl halides <sup>115, 116, 405</sup> or sulfates, <sup>265, 362</sup> or aryl halides. <sup>115, 116, 373</sup> Two thiophene sulfide-acids,  $\text{C}_4\text{H}_3\text{S}\cdot\text{SC}_6\text{H}_4\text{CO}_2\text{H}$ , have been prepared from 3-bromothiophene and 2-iodothiophene and thiosalicylic acid. <sup>402, 403</sup>

An active halide may react with thioglycolic amide in the absence of alkali: <sup>392</sup>



In some cases an alcohol can be made to react with thioglycolic acid:



This condensation takes place in the presence of an acid catalyst, such as dilute hydrochloric acid at  $100^\circ$ . This applies to alcohols in which the hydroxyl is labile, <sup>224</sup> such as benzyl, <sup>205d, 407b</sup>  $\alpha$ -methylbenzyl, <sup>208b, 206c, 209b</sup> phenethyl, and cinnamyl <sup>205d, 206b</sup> alcohols, triphenylcarbinol, <sup>205d</sup> *t*-butanol, <sup>16, 187</sup> benzhydrol, <sup>103, 205d</sup> benzoin, <sup>31, 419b</sup> a methanolamide,  $\text{RCONHCH}_2\text{OH}$ , <sup>391b</sup> and lactic acid. <sup>270c</sup>

#### ADDITION OF A MERCAPTAN TO AN UNSATURATED ACID

The simplest synthesis of a sulfide-acid is the addition of a mercaptan to an unsaturated acid:



The same end result is achieved by starting with acrylonitrile, which is more reactive, and saponifying the nitrile. The addition product of thiophenol and acrylic acid<sup>335c</sup> has been shown to be identical with that synthesized from thiophenol and  $\beta$ -chloropropionic acid in alkaline solution. The sulfone of this acid proved to be identical with the sulfone acid from the addition of benzenesulfinic acid to acrylic acid.<sup>212b</sup>

Ethyl mercaptan<sup>335c</sup> and *p*-thiocresol<sup>318b</sup> have been added to cinnamic acid. With ethyl mercaptan the reaction required several weeks at room temperature.<sup>335c</sup> Ethyl mercaptan is usually rather sluggish but it combines with methyl acrylate in the presence of ascaridole and ultraviolet light or of trimethylbenzylammonium hydroxide. The product is methyl  $\beta$ -ethylmercapto-propionate,  $\text{EtSCH}_2\text{CH}_2\text{CO}_2\text{Me}$ .<sup>243</sup> Mercaptans have been added to acrylic,<sup>33, 94, 217b, 235</sup> maleic,<sup>87, 217b, 235, 310a, 444</sup> methacrylic,<sup>62, 217b</sup>  $\beta,\beta$ -dimethylacrylic<sup>408</sup> and crotonic<sup>84, 324</sup> acids, and also to the ketoacids,  $\text{PhCOCH:CHCO}_2\text{H}$ ,<sup>51</sup>  $\text{PhCH:CHCOCO}_2\text{H}$ ,<sup>318b</sup> and 6-oxo-7-octenoic acid.<sup>393</sup> The addition of an anti-oxidant to prevent polymerization has been claimed.<sup>217b</sup> The addition reaction may be catalyzed by pyridine.<sup>334b</sup>  $\beta$ -Mercaptoethanol has been added to dioleyl maleate.<sup>40</sup> The reaction of benzyl mercaptan with  $\alpha$ -nitro- $\beta$ -methylcrotonic ester is highly exothermic.<sup>5, 141</sup> It adds to the  $\beta$ -methylcrotonic ester in the presence of pyridine.<sup>5, 93</sup> This mercaptan has been added to ethyl acrylate, to acrylonitrile, and to maleic anhydride.<sup>413</sup> A number of aliphatic and aromatic mercaptans have been added to acrylonitrile and to methyl acrylate with the aid of a basic catalyst.<sup>215, 404</sup>

*p*-Thiocresol has been added to acrylonitrile and to methyl acrylate and  $\beta$ -thionaphthol to acrylonitrile.<sup>292</sup> 3-Thiophenethiol and maleic anhydride give 3-thienylmercaptosuccinic acid.<sup>59</sup> Unless the mercaptan is an active one a catalyst, such as sodium methylate, is required.<sup>345</sup> Decyl, dodecyl, and octadecyl mercaptans have been added to acrylonitrile in this way.<sup>384</sup> In alkaline solution, 2-mercaptobenzothiazole combines with it readily.<sup>181</sup> Thiophenol has been added to several  $\beta$ -alkylacrylonitriles.<sup>359</sup> With active mercaptans, acrylonitrile requires no catalyst. In the absence of any known catalyst its reaction with ethanedithiol is spontaneous and so highly exothermic that the one must be run into the other, slowly and with efficient cooling.<sup>351</sup>

The addition of a sulfenyl chloride to ketene gives the chloride of a sulfidoacetic acid: <sup>356</sup>



With an unsaturated acid the addition product is a chloro-acid: <sup>58</sup>



Mercaptans have been added to the benzaldehyde-anthranilic acid Schiff's base: <sup>396</sup>



Though the products are sulfides and also acids, they are not sulfide-acids since the sulfur and the carboxyl are not attached to the same carbon chain.

#### ADDITION OF A MERCAPTO-ACID TO AN UNSATURATE

Of all mercapto-acids, thioglycolic is the one that has been used most frequently in these additions. It is readily available and is exceptionally reactive. Reference should be made to chapter 5, Volume I, on mercapto-acids. The rate of addition of this acid to various olefins under a variety of conditions has been studied. The reaction goes well in alcohol and in acetic acid and particularly so in propionic.<sup>213</sup> The addition may take place quickly with the evolution of considerable heat or may require many hours at room temperature.<sup>205a</sup> The influence of para substituents in  $\alpha$ -methylstyrene on the rate of addition of thioglycolic acid to it has been investigated. A halogen decreases the rate somewhat; a methyl group doubles it, while a methoxyl increases it a hundred fold.<sup>430</sup> When thioglycolic acid is mixed with a higher unsaturated alcohol, or with its ester, the temperature must be kept low so that the reaction is limited to addition at the double bond.<sup>113</sup> The addition goes particularly well when an open vinyl group,  $-\text{CH}:\text{CH}_2$ , is present as in the alpha olefins, decene-1, dodecene-1, tetradecene-1,  $\beta$ -pinene, and undecylenic acid.<sup>189c, 190c, 320, 391a</sup> Thioglycolic acid adds spontaneously to  $\alpha$ -terpineol, terpinolene, and vinyl acetate.<sup>351</sup> When one mole of thioglycolic acid was mixed with one of allyl alcohol the temperature rose  $22^\circ$  within 5 minutes. When 25 g. of it was poured into 40 g. of undecylenic acid the temperature went up

68° within about one minute and, on cooling, the product set to a solid mass of crystals.<sup>351</sup>

The addition of mercapto-acids, as that of mercaptans, to unsaturates goes contrary to Markownikow's rule, which appears to be due to the presence of peroxides. The amounts of these which are required are so small that the traces which are usually present in organic compounds, that have been exposed to the air, are sufficient. It is inhibited by hydroquinone.<sup>244</sup> Sulfur usually retards the reaction and may reverse the mode of addition but this requires further investigation.<sup>351</sup> The addition of thioglycolic acid to cyclohexene,<sup>100, 437a</sup> 1-methylcyclohexene,<sup>100, 188</sup> 4-methylcyclohexene,<sup>188</sup> and dihydromyrcene takes place spontaneously. If these hydrocarbons have been freshly distilled there is no addition. The reaction is almost explosive in the presence of ascaridole.<sup>100</sup> Addition to dicyclopentadiene has been reported.<sup>63</sup>

From thioglycolic acid, safrole, and isosafrole, in the presence of ascaridole, the two acids,  $C_7H_5O_2 \cdot CH_2CH_2CH_2SCH_2CO_2H$  and  $C_7H_5O_2 \cdot CH_2CHMeSCH_2CO_2H$ , have been prepared.<sup>338</sup> If iodine is substituted for the ascaridole, the addition goes according to Markownikow's rule and the product from isosafrole is  $C_7H_5O_2 \cdot CHEtSCH_2CO_2H$ .<sup>412</sup> The reaction of the iodine with some of the mercaptan produces hydroiodic acid and it is well known that the acid-catalyzed addition goes according to this rule.

Benzalacetophenone,  $PhCH:CHCOPh$ , and sodium thioglycolate, in alkaline alcohol solution, combine to form benzylacetophenone- $\beta$ -thioglycolic acid.<sup>318a</sup>  $\beta$ -Mercaptopropionic acid has been added to styrene to give the acid,  $PhCH_2CH_2SCH_2CH_2CO_2H$ .<sup>209b</sup>

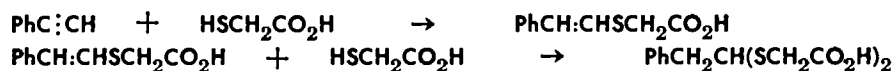
When ethyl thioglycolate, butylideneacetonitrile,  $PrCH:-CHCN$ , and sodium ethylate are heated together, addition and condensation take place to form 2-propyl-3-cyano-4-keto-tetrahydrothiophene. A number of thiophane derivatives related to biotin have been prepared similarly.<sup>18, 19, 60, 61, 443</sup> Reference should be made to chapter 1.

Thioglycolic acid can be added to allylsilicon derivatives,  $CH_2:CHCH_2SiMe_3$ ,  $CH_2:CHCH_2SiOSiMe_3$  and  $CH_2:CHCH_2Si(OEt)_3$ .<sup>57, 67, 68, 272a</sup>

The acids,  $PhSO_2CH_2CH_2SCH_2CO_2H$  and  $PhSO_2CH_2CH_2SC_6H_4CO_2H$ -o, have been prepared by adding thioglycolic and thiosalicylic acids to phenyl vinyl sulfone.<sup>144</sup> Thioglycolic acid

adds to divinyl sulfone to form the acid,  $\text{O}_2\text{S}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H})_2$ .<sup>351</sup>

Thioglycolic acid can be added to phenylacetylene in two stages:

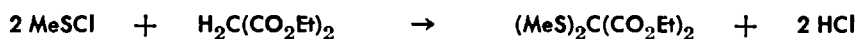


There are two forms of the first addition product, both of which melt at  $90^\circ$  but melt at  $64-7^\circ$  when mixed.<sup>210</sup> A mercapto-acid has been added to diacetylene.<sup>83</sup>

Chloranil and thioglycolic acid give 2,3,5,6-tetra(carboxymethylmercapto)hydroquinone, 1,4,2,3,5,6-(HO)<sub>2</sub>C<sub>6</sub>(SCH<sub>2</sub>COOH)<sub>4</sub>, m.  $289^\circ$ . This is partly addition and partly substitution.<sup>380b</sup> Addition is probably the first step in the reaction of thioglycolic acid, or  $\beta$ -mercaptopropionic acid, with quinone to give hydroquinone- $\alpha$ -thioacetic acid and lactone or hydroquinone- $\beta$ -thiopropionic acid.<sup>390</sup>  $\beta$ -Mercaptopropionic acid reacts similarly with naphthoquinone.<sup>178</sup>

#### OTHER METHODS OF PREPARATION

If the alkyl halide that is used in the synthesis of an acid is a sulfide, the resulting acid will be a sulfide-acid. Thus the sulfide-chloride,  $\text{MeSCH}_2\text{CH}_2\text{Cl}$ , has been used with malonic ester for preparing the acid,  $\text{MeSCH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{H})_2$ , as an intermediate in the synthesis of methionine.<sup>440</sup> Starting with acetylamino-malonic ester shortens the path to this goal.<sup>165</sup> This will be considered further in the chapter on methionine. From monosubstituted malonic esters and chloromethyl alkyl sulfides,  $\text{RSCH}_2\text{Cl}$ , a number of disubstituted malonic esters,  $\text{RSCH}_2\text{R}'\text{C}(\text{CO}_2\text{Et})_2$ , have been made as intermediates for barbituric acids.<sup>45, 431, 432</sup> Alkylmercaptobarbituric acids,  $\text{R}'\text{SCR}(\text{CONH})_2\text{CO}$ , have been prepared from a mercaptide and bromobarbituric acid,  $\text{BrCR}(\text{CONH})_2\text{CO}$ .<sup>175</sup> Methanesulfonyl chloride introduces two methylmercapto groups into malonic ester:<sup>56</sup>



Triethyltrithioorthoformate condenses with malonic ester to  $\text{EtSCH}:\text{C}(\text{CO}_2\text{Et})_2$ .<sup>176</sup> A sulfide-keto-acid,  $\text{MeCOCH}(\text{SMe})\text{CO}_2\text{H}$ , can be made by treating acetoacetic ester with methanesulfonyl chloride.<sup>56</sup>



$\beta$ -Mercaptopropionic ester reacts with ethylene imine to form the ester,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{Et}$ .<sup>39</sup>

A methylmercaptoaniline,  $\text{RSC}_6\text{H}_4\text{NH}_2$ , may be diazotized and converted to the nitrile which is hydrolyzed. Examples are  $p\text{-PrSC}_6\text{H}_4\text{CO}_2\text{H}$ ,  $p\text{-BuSC}_6\text{H}_4\text{CO}_2\text{H}$ ,<sup>72</sup> and  $m\text{-MeSC}_6\text{H}_4\text{CO}_2\text{H}$ .<sup>44b</sup>

A metal derivative of a sulfide may give an acid:<sup>164</sup>



By the Friedel and Crafts reaction thioanisole has been converted to the acids,  $p\text{-MeSC}_6\text{H}_4\text{COCH}_2\text{CH}_2\text{CO}_2\text{H}$ <sup>71, 73</sup> and  $p\text{-MeSC}_6\text{H}_4\text{COCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ ,<sup>73</sup> which have been reduced to methylmercaptophenylbutyric and methylmercaptophenylvaleric acids.

$p$ -Methylmercaptoacetophenone has been converted to methylmercaptophenylacetic acid by the Willgerodt reaction. Phenylmercaptophenylacetic acid has been made similarly.<sup>95</sup>

## Reactions

### WITH METAL SALTS

Methyl-<sup>186</sup> and ethyl-<sup>342b, 342d</sup> mercaptoacetic acids,  $\text{MeSCH}_2\text{CO}_2\text{H}$  and  $\text{EtSCH}_2\text{CO}_2\text{H}$ , form complexes with salts of mercury<sup>186</sup> and platinum.<sup>342b, 342d</sup> Ethylthiolactic acid,  $\text{EtSCHCH}_3\text{CO}_2\text{H}$ , which has been resolved, gives similar complexes.<sup>281</sup>  $o$ -Methylmercaptobenzoic acid gives palladium complexes.<sup>282, 283</sup> Conductivity measurements on solutions of silver nitrate, in the presence of various sulfide-acids, show the presence of complex ions. The equilibrium constants for these have been calculated.<sup>273d</sup>

Certain sulfide-acids, such as  $\alpha$ -phenylethylmercaptoacetic,  $\text{PhCHMeSCH}_2\text{CO}_2\text{H}$ , in which the alkyl-sulfur bond is not strong, are split by heating with hydrochloric acid and mercuric chloride.<sup>208a, 208c, 209c</sup>

### HYDROLYSIS

Sulfides and sulfide-acids are hydrolyzed by alkali with great difficulty<sup>223, 224, 225</sup> unless there is a hydroxyl<sup>270c</sup> or keto group on an adjoining carbon atom.<sup>29, 31, 419a</sup> A mercaptan may be split off:<sup>318a, 376</sup>



On standing in sodium carbonate solution, (3,5-diiodo-4-pyridyl-mercapto)-acetic acid is hydrolyzed to the mercaptan which is oxidised to the disulfide.<sup>252</sup> 1-Methyl-5-chlorobenzene-2-carboxyl-amino-3-thioglycolic acid is converted to a thioindigo intermediate by treatment with alkali.<sup>201</sup>

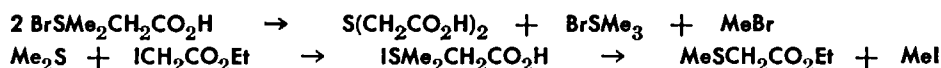
Triphenylmethyl sulfide-acids,  $\text{Ph}_3\text{CS}(\text{CH}_2)_n\text{CO}_2\text{H}$ , are unaffected by alkali but are hydrolyzed by cold, concentrated sulfuric acid.<sup>222</sup>

### SULFONIUM

Chloroacetic<sup>262</sup> and bromoacetic acids form sulfonium compounds with alkyl sulfides:



This decomposes on heating: <sup>262, 279, 280</sup>



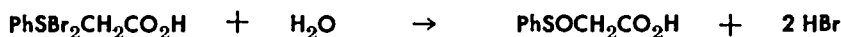
A sulfonium compound is formed as well by the addition of an alkyl halide to a sulfide-acid.<sup>206c, 362, 437b</sup> Bromoacetic acid may add to a sulfide-acid.<sup>208a</sup> A study has been made of the kinetics of these reactions.<sup>185c</sup>

### OXIDATION

In anhydrous solvents sulfide-acids take up bromine: <sup>340a</sup>



In some cases substitution also takes place.<sup>157</sup> The bromine addition product is hydrolyzed readily:

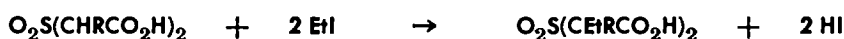


Oxidation of sulfide- to sulfoxide-acids may be effected by hydrogen peroxide,<sup>208c, 232</sup> oxides of nitrogen,<sup>340b</sup> or by sodium bromate. Some of the sulfoxides go to the sulfones readily, others not so readily.<sup>271a, 271c, 272a</sup> A study has been made of the kinetics of the oxidation of sulfide-acids.<sup>272b</sup>

Further oxidation gives the sulfone-acids. Potassium permanganate has been the agent most commonly employed.<sup>3a, 16, 41, 140b, 232, 250a, 250b, 271d, 286a, 287a, 288, 289, 312, 335c, 342a, 353b, 353c, 371, 407b</sup> Recently hydrogen peroxide has come into wide use.<sup>33, 91, 117,</sup>

130, 177, 212b, 334a, 371, 424 With it the oxidation can be carried to the sulfoxide or sulfone stage by adjusting the amount used and regulating the temperature.<sup>134, 140b, 153, 187, 195b, 212b, 233, 270d, 271c, 276a, 322, 340b, 406, 407b, 434</sup>

The sulfone-acid,  $\text{O}_2\text{S}(\text{CHMeCO}_2\text{H})_2$ , is inactive regardless of whether it is made from the racemic or an active thiolactic acid.<sup>288</sup> An  $\alpha$ -sulfone-acid can be alkylated in alkaline solution: <sup>286a</sup>

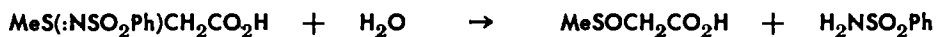


### OTHER REACTIONS

Sulfide-acids can be esterified by conventional methods.<sup>101, 189e, 190a, 202, 305, 306</sup> The esterification velocities of the acids,  $\text{MeSCH}_2\text{CO}_2\text{H}$ ,  $\text{EtSCH}_2\text{CO}_2\text{H}$ ,  $\text{MeSCH}_2\text{CH}_2\text{CO}_2\text{H}$ , and  $\text{EtSCH}_2\text{CH}_2\text{CO}_2\text{H}$  are lower than those of propionic, butyric, and valeric acids.<sup>326</sup> The saponification rate of ethyl benzoate is markedly influenced by the introduction of the methylmercapto group in the meta or para position.<sup>245, 336</sup> Polyethyleneglycol esters,  $\text{RSCH}_2\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ , obtained by the action of ethylene oxide on an alkylmercaptoacetic acid, are said to be useful for several purposes.<sup>260, 261</sup>

*m*-Butylmercaptobenzoic acid is converted to the chloride by sulfonyl chloride. From this the methyl ester, the amide and the *N*-diethylaminoethylamide have been prepared.<sup>291</sup>  $\beta$ -Naphthylmercaptomethylurea,  $(\beta\text{-C}_{10}\text{H}_7\text{SCH}_2\text{N})_2\text{CO}$ . Di-*p*-tolylmercaptomethylurea is made similarly.<sup>248</sup> 2-Pyridylmercaptoacetic acid and 2-quinoylmercaptoacetic acid are converted to anhydro compounds by heating with acetanhydride.<sup>119</sup>

The sulfilimine of methylmercaptoacetic acid is hydrolyzed to the sulfoxide:



The sulfoxide splits into the mercaptan and aldehyde which combine to form the acetal:

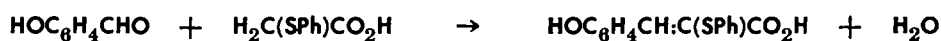


Similar reactions take place with sulfilimines of other alkylmercaptoacetic acids.<sup>415</sup>

The chlorination of methyl methylmercaptoacetate gives the dichloride which is hydrolyzed to the monothio-oxalic ester:

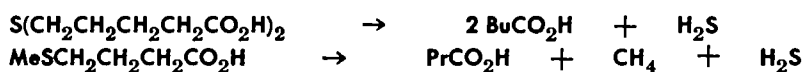


An ester of an  $\alpha$ -sulfide-acid can be alkylated by treatment with sodium and methyl iodide, though not as readily as the sulfone which has been mentioned above. Thus  $\text{PhSCH}_2\text{CO}_2\text{Et}$  is changed to  $\text{PhSCHMeCO}_2\text{Et}$ .<sup>340b</sup> The Perkin condensation may take place between an aromatic aldehyde and phenylmercaptoacetic acid:



This cinnamic acid can be reduced to the hydrocinnamic.<sup>328</sup>

Under extreme conditions, sulfide-acids undergo hydrogenolysis: 49, 311



The sulfide-acid chlorides,  $\text{PhCH}_2\text{CH}_2\text{SCH}_2\text{COCl}$  and  $\text{PhCH}_2\text{-CH}_2\text{CH}_2\text{SCH}_2\text{COCl}$ , are converted to cyclic ketosulfides by aluminum chloride in carbon disulfide.<sup>53</sup> The acid,  $p\text{-BrC}_6\text{H}_4\text{-SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , is converted to 6-bromo-4-thiachromanone by concentrated sulfuric acid,<sup>74</sup> the nitro acid,  $p\text{-O}_2\text{NC}_6\text{H}_4\text{SCH}_2\text{-CH}_2\text{CO}_2\text{H}$ , requires this and phosphoric anhydride for cyclization.<sup>35</sup>  $\gamma$ -Phenylmercaptobutyryl chloride,  $\text{PhSCH}_2\text{CH}_2\text{CH}_2\text{-COCl}$ , is converted to 5-thiahomochromanone by aluminum chloride.<sup>75</sup> The acid,  $m\text{-C}_6\text{H}_4(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , is converted to thiopyrone by concentrated sulfuric acid.<sup>137</sup> Benzhydrylmercaptothioacetamide,  $\text{Ph}_2\text{CHSCH}_2\text{CSNH}_2$ , and ethylene diamine give 2-(benzhydrylthiomethyl)imidazoline.<sup>102</sup>

### Applications

The alkali salts of long chain acids, such as  $\text{C}_{12}\text{H}_{25}\text{SCH}_2\text{CO}_2\text{H}$ , have saponaceous and emulsifying properties.<sup>124, 125, 189b, 190a, 190b, 190d, 191, 429</sup> The lithium salts of acids of this type, containing silicon in the alkyl, are said to have these properties.<sup>68</sup> Acids of the type,  $\text{H(CH}_2)_m\text{S(CH}_2)_n\text{CO}_2\text{H}$ , in which  $m$  and  $n$  may be 3 to 9, improve the wetting properties of mercerizing lyes.<sup>123, 217d</sup> The sodium salts,  $\text{C}_{11}\text{H}_{23}\text{CONHCH}_2\text{SCH}_2\text{CO}_2\text{Na}$  and  $\text{C}_{17}\text{H}_{35}\text{-CONHCH}_2\text{SCH}_2\text{CO}_2\text{Na}$ , give foaming solutions which are useful

with textiles.<sup>391b</sup> The alkali salts of phenylmercaptosuccinic acids are detergents.<sup>339</sup> Long chain esters of the type,  $\text{RSCH}_2\text{CO}_2\text{R}'$ , are emulsifying agents when the R contains a water-solubilizing group.<sup>290</sup> Sulfide-acids having amide linkages in the chain<sup>364</sup> and acids,  $\text{RS}(\text{CH}_2)_3\text{CO}_2\text{H}$ , in which R is ethyl, phenyl, *p*-tolyl, or  $\beta$ -naphthyl,<sup>15</sup> are claimed to be useful in textile auxiliary agents. Amides of sulfide-acids are said to be useful in printing on fibrous materials.<sup>391c</sup>

The addition products of thiophenol to esters of acrylic and  $\alpha$ -alkylacrylic acids are useful plasticizers.<sup>226</sup> The same is true of esters of sulfide-acids with higher alcohols, such as  $\text{PhSCH}_2\text{CO}_2\text{C}_{12}\text{H}_{25}$ .<sup>193</sup> The butyl and 2-ethylhexanol esters of benzothiazolylmercaptoacetic acid are claimed as plasticizers for polyvinyl chloride.<sup>107</sup> Acids of the type  $\text{RSCHR}'\text{CO}_2\text{H}$ , in which R is a terpene radical and R' is either alkyl or aryl, are proposed as milling aids for GR—S polymers.<sup>428</sup>

Esters of 3-thienylmercaptoacetic acid and the like are claimed as additions for lubricants.<sup>58</sup> Glycol esters of sulfide-acids serve the same purpose.<sup>389</sup> Sulfide-acids, such as  $\alpha$ -amylmercaptostearic, inhibit oxidation of lubricating oils.<sup>70, 357</sup> The cetyl<sup>433, 434</sup> and octadecyl<sup>434</sup> acids,  $\text{C}_{16}\text{H}_{33}\text{SCH}_2\text{CO}_2\text{H}$  and  $\text{C}_{18}\text{H}_{37}\text{SCH}_2\text{CO}_2\text{H}$ , inhibit rust formation.

Sulfide-acids and their esters are recommended for removing traces of heavy metals from edible animal or vegetable oils.<sup>174a</sup> Salts of certain sulfide-acids are solutizers.<sup>1, 333</sup>

Some substituted phenylmercaptoacetic acids are herbicides;<sup>127</sup> others are pesticides;<sup>231</sup> others have been tested as plant growth regulators.<sup>315, 420</sup> Certain antimony derivatives are trypanocides.<sup>398</sup> Diethylaminoethyl *p*-ethylmercaptocinnamate and 3-ethylmercapto-4-hydroxybenzoate are more effective than procaine or cocaine as local anesthetics.<sup>263</sup>

## Dibasic Sulfide-Acids

### THIODIGLYCOLIC ACID

The simplest of these, thiodiglycolic acid,  $\text{S}(\text{CH}_2\text{CO}_2\text{H})_2$ , was prepared for the first time from chloroacetic acid and lead sulfide<sup>160</sup> and its amide from chloroacetamide and ammonium sulfide.<sup>381a</sup> Calcium<sup>379</sup> and potassium<sup>6</sup> sulfides were used in later preparations. The ethyl ester was obtained starting with ethyl

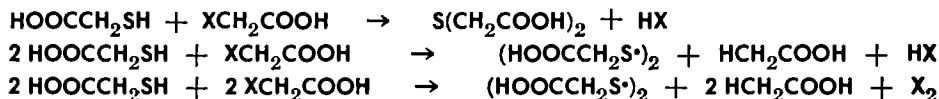
chloracetate.<sup>183</sup> The sulfide-acid was found as a by-product in making thioglycolic acid.<sup>77, 250c, 441</sup>

To prepare thiodiglycolic acid a solution of 1320 g. of sodium sulfide,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , in 850 cc. of water is added slowly, with ice cooling, to 945 g. chloracetic acid, in 1500 cc. of water, that has been neutralized with sodium bicarbonate. After standing at  $0^\circ$  for an hour 750 cc. of concentrated sulfuric acid is added keeping the temperature below  $35^\circ$ . The acid is taken out by ether in a continuous extractor. The yield may be near 90%.<sup>22, 114, 286a, 286b</sup> Cyclohexanone and the alcohols, propyl to hexyl, are recommended for extracting the acid from the aqueous solution.<sup>26</sup> Extraction by methyl ethyl ketone is aided by salting out.<sup>92</sup>

Thiodiglycolic acid may also be made from a salt of thioglycolic acid and a halogen acetic acid:



The reaction follows the bimolecular law but the velocity depends on the nature of the cation. The variations are great. Three different reactions may take place: <sup>184c, 185a, 185b</sup>



Two equivalents of triethylamine may be added to one of thioglycolic acid in dry benzene and then octyl chloroacetate added. After heating the mixture the amine hydrochloride is filtered off.<sup>145</sup>

Thiodiglycolic esters of the higher alcohols, such as butyl, amyl, hexyl,<sup>266</sup> and dodecyl,<sup>189a, 190b</sup> have been prepared from the corresponding esters of chloroacetic acid. The nitrile,  $\text{S}(\text{CH}_2\text{CN})_2$ , and the amide,  $\text{S}(\text{CH}_2\text{CONH}_2)_2$ , can be made from chloroacetonitrile and ammonium sulfide.<sup>399, 400, 448</sup> The thioamide,  $\text{S}(\text{CH}_2\text{CSNH}_2)_2$ , is formed when chloroacetonitrile is added to an alcoholic solution of ammonia saturated with hydrogen sulfide.<sup>448</sup>

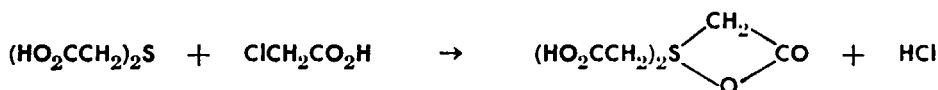
The acid chloride can be made by adding sulfur dichloride to ketene, or to a substituted ketene: <sup>179, 320, 321</sup>



The dissociation constant of thiodiglycolic acid has been compared with those of other acids.<sup>273a, 284, 323, 436, 439</sup> This acid is

less reactive than its oxygen analog,  $O(CH_2CO_2H)_2$ , but the reverse is true of thioglycolic and glycolic acids.<sup>331</sup>

Thiodiglycolic acid forms a sulfonium complex with chloroacetic acid: <sup>111c</sup>



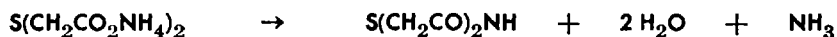
It forms complexes with cobalt salts and amines<sup>337</sup> and with lead, silver, and mercury salts.<sup>118</sup> Its acid platinum salt has been described.<sup>342b</sup>

Thiodiglycolic acid has been compared, as to toxicity, with thioglycolic, dithiodiglycolic, and with a variety of other compounds.<sup>109</sup> Its effect on the nitrogen balance in sheep has been studied.<sup>135</sup>

Thiodiglycolic acid may be esterified by an alcohol and the usual catalysts.<sup>27</sup> The rates of formation and of hydrolysis of its esters,  $S(CH_2CO_2R)_2$ , have been compared with those of the corresponding oxygen compounds,  $O(CH_2CO_2R)_2$ , and with glutaric esters,  $CH_2(CH_2CO_2R)_2$ .<sup>327</sup>

The diethyl ester condenses with ethyl oxalate to the ester of 3,4-dihydroxythiophene-2,5-dicarboxylic acid.<sup>198</sup> Similar reactions take place with  $MeCO \cdot COPh$  and with glyoxal. The products from these are 3-methyl-4-phenylthiophene-2,5-dicarboxylic<sup>11</sup> and thiophene-2,5-dicarboxylic acids.<sup>198</sup>

Thiodiglycolic acid is converted by two molecules of phosphorus pentachloride into the acid chloride,  $S(CH_2COCl)_2$ , from which the dimethyl ester and dianilide have been prepared.<sup>7</sup> Refluxing the acid with acetic anhydride<sup>269</sup> or with acetyl chloride, or treating it with one molecule of phosphorus pentachloride, gives the anhydride,  $S(CH_2CO)_2O$ .<sup>7</sup> With aniline this forms the monoanilide, or anilic acid, which goes into the N-phenylimide,  $S(CH_2CO)_2NPh$ , on heating.<sup>7, 346</sup> When the diammonium salt is heated to  $200^\circ$ ,<sup>381b</sup> or when its aqueous solution is evaporated in a vacuum and the residue is distilled the imide is obtained:



When the vapor of this imide is passed over pumice coated with alumina, it is converted into 1,4-thiazine,  $S(CH:CH)_2NH$ .<sup>22</sup> The anilide can be benzoylated to  $S(CH_2CONBzPh)_2$ .<sup>423</sup> Resorcinol

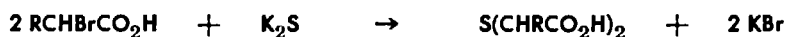
and phloroglucinol condense with thiodiglycolic acid to thiodiglycoleins.<sup>114</sup>

Polymeric condensation products of thiodiglycolic acid with diamines, such as decamethylene diamine,<sup>182</sup> or with glycols,<sup>219</sup> are said to be useful. The propyl, butyl, amyl, and cyclohexyl esters are claimed as plasticizers.<sup>42</sup>

Treating thiodiglycolic acid with sodium hypochlorite and hydrochloric acid gives hexachlorodimethyl sulfone,  $\text{O}_2\text{S}(\text{CCl}_3)_2$ .<sup>228</sup>

### HOMOLOGS OF THIODIGLYCOLIC ACID

The symmetrical acids are from the haloacids and an alkali sulfide:



The most available halogen acids are those having the halogen in the  $\alpha$ -position. The best known acid of this class is thiodilactic acid, which was first obtained as a by-product in the preparation of thiolactic acid,  $\text{MeCH}(\text{SH})\text{CO}_2\text{H}$ .<sup>286a, 287a</sup> This acid,  $\text{S}(\text{CHMeCO}_2\text{H})_2$ , has been resolved by quinine into two active forms,  $[\alpha]197^\circ$  and  $-198^\circ$ . Both of these melt at  $117^\circ$  and a mixture of the two at  $127^\circ$ .<sup>146d, 147a</sup> The  $\beta, \beta'$ -thiodipropionic acid,  $\text{S}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2$ ,<sup>286d</sup> is best made from  $\beta$ -bromopropionic acid.<sup>36</sup>

From  $\alpha$ -bromobutyric,  $\alpha$ -bromo-*i*-butyric,  $\beta$ -bromobutyric and  $\beta$ -bromo-*i*-butyric acids the isomeric acids,  $\text{S}(\text{CHEtCO}_2\text{H})_2$ ,<sup>3a, 3c, 287a</sup>  $\text{S}(\text{CMe}_2\text{CO}_2\text{H})_2$ ,<sup>195a, 195b, 273c, 276a, 287a</sup>  $\text{S}(\text{CHMeCH}_2\text{CO}_2\text{H})_2$ ,<sup>8, 289, 367</sup> and  $\text{S}(\text{CH}_2\text{CHMeCO}_2\text{H})_2$ ,<sup>273c, 276b</sup> have been prepared.

The meso  $\alpha, \alpha'$ -thiodi-*i*-valeric acid,  $\text{S}[\text{CH}(\text{CO}_2\text{H})\text{CHMe}_2]_2$ , is partially changed to the racemic form on heating. This has been resolved,  $[\alpha]22/\text{D} -126.5^\circ$  and  $[\alpha]18/\text{D} 129$ .<sup>3a</sup> The  $\delta, \delta'$ -acid also is known.<sup>221, 272c</sup>

The  $\alpha$ -bromo derivatives of the higher fatty acids react satisfactorily with sodium sulfide.<sup>251</sup> A halogenated nitrile is frequently the starting material.<sup>41, 78, 79, 154b, 314</sup>

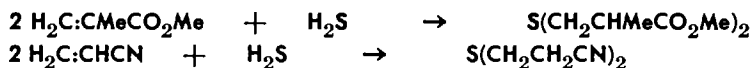
The sulfide ester,  $(\text{MeO}_2\text{C})_2\text{CHSCH}(\text{CO}_2\text{Me})_2$ , has been made from methyl malonate and sulfur monochloride. The disulfide ester,  $(\text{MeO}_2\text{C})_2\text{CHSSCH}(\text{CO}_2\text{Me})_2$ , was a by-product.<sup>442</sup> The  $\gamma, \gamma'$ -thiodibutyric acid,  $\text{S}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , has been synthesized from acetoacetic ester and from malonic ester with



dichloroethyl sulfide.<sup>105</sup> The ketosulfide ester,  $S[CH(COMe)-CO_2Et]_2$ , has been obtained from acetoacetic ester with sulfur monochloride<sup>64, 259</sup> or dichloride<sup>65, 111a, 111b, 395</sup> or with thionyl chloride.<sup>302</sup> The copper salt of acetoacetic ester and sulfur give the same ester.<sup>377</sup> This sulfide acetoacetic ester is readily enolized.<sup>255</sup>

Useful products are said to be obtained by treating poly-halogenated fatty acids with metal sulfides or polysulfides.<sup>217c</sup>

A symmetrical sulfide-acid can be obtained by the addition of hydrogen sulfide to an unsaturated acid or nitrile. This goes particularly well with an acrylic ester or acrylonitrile. It is aided by the presence of a basic catalyst, such as an amine or a tetra-alkylammonium hydroxide, such as  $PhCH_2NMe_3OH$ ; <sup>66, 82, 131, 161, 180, 204, 218</sup>



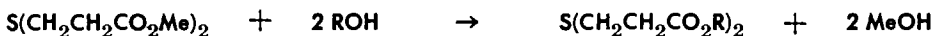
Acrylic acid is added to a hot solution of sodium sulfide, kept at pH 9.<sup>108</sup> Hydrogen sulfide unites with methyl acrylate in the presence of sodium sulfide.<sup>133b</sup> The sulfide-nitrile,  $S(CH_2CH_2CN)_2$ , is obtained by stirring acrylonitrile and viscose together for 3 hours.<sup>293</sup> A sulfur chloride may be added to an unsaturated acid.<sup>37</sup>

$\beta$ -Propiolactone reacts with  $\beta$ -mercaptopropionic acid, in alkaline solution, to give  $\beta, \beta'$ -thiodipropionic acid but the  $\beta$ -mercaptopropionic acid is from this lactone and hydrogen sulfide, likewise in alkaline solution. Hence, the final product may be obtained in one operation by treating two molecules of the lactone with one of sodium sulfide.<sup>166a, 170, 172a, 172b</sup>  $\gamma$ -Butyrolactone reacts similarly.<sup>13, 14, 319</sup>

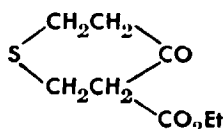
Thiodipropionic acid can be titrated, as a sulfide, with standard bromide-bromate solution.<sup>184a, 270d</sup> The sulfinylo-acid can serve as an oxidising agent:



When heated with hydrochloric acid, disproportionation takes place with the formation of some of the sulfonyl acids,  $O_2S(CH_2CH_2CO_2H)_2$ .<sup>270b, 270d</sup> The esters of thiodipropionic acid undergo alcoholysis with phosphoric acid as a catalyst:<sup>173</sup>



Plastics may be obtained by esterifying it with glycols.<sup>217a</sup> Certain of its higher esters are claimed as stabilizers for polythene,<sup>174b</sup> others are plasticizers.<sup>108</sup> The diethyl ester can be condensed by sodium ethylate to the cyclic keto-ester:



The free acid can be decarboxylated to the ketone, penthianone-4,  $S(CH_2CH_2)_2CO$ ,<sup>36</sup> which has been mentioned in chapter 1.

Two sulfide-acids,  $S[CMe(OH)CO_2H]_2$  and  $S[CMe(SH)CO_2H]_2$ , have been identified among the products of the treatment of pyruvic acid with hydrogen sulfide.<sup>47, 110, 287b</sup>

Various esters of sulfide-acids are claimed as plasticizers.<sup>316, 317, 319, 366</sup> The 2-ethylhexanol ester of thiodibutyric acid is said to be the best plasticizer for polyvinyl chloride.<sup>361</sup> Additives for lubricating oils are said to have been made by treating esters of aliphatic acids with sulfur chloride.<sup>37</sup> Various useful products have been made from  $\alpha, \alpha'$ -thiodibutyrolactone.<sup>13</sup> Sulfide-acids such as  $\alpha, \alpha'$ -thiodilauric are reported as preventing corrosion, even by salt water. Very small percentages of them in mineral oil are effective.<sup>447</sup>

The dissociation constants of the acids,  $HO_2C(CH_2)_nS(CH_2)_nCO_2H$ , in which  $n = 1, 2$ , or  $3$ , have been measured.<sup>2</sup>

When hydrogen chloride is passed into an aqueous solution of  $\beta, \beta'$ -thiodipropionic and acrylic acids the sulfonium chloride,  $(HO_2CCH_2CH_2)_3S^+Cl^-$ , is formed.<sup>374</sup>

#### SYMMETRICAL THIODIBENZOIC ACIDS

2,2'-Thiodibenzoic acid has been made from *o*-chlorobenzoic acid and cuprous thiocyanate in pyridine. *o*-Bromobenzoic acid gives better results.<sup>358</sup> The same acid has been obtained from *o*-chlorobenzoic acid and thiosalicylic acid.<sup>296</sup>

5,5'-Thiodisalicylic acid has been made by the action of sulfur dichloride on sodium acetyl salicylate<sup>4</sup> or of thionyl chloride, sulfur dichloride, or sulfur monochloride on the methyl ester in the presence of copper.<sup>199</sup> It has been obtained from salicylic acid with the aid of certain cultures of bacteria. Many derivatives have been prepared, esters, aminoalkyl esters, and *N*-alkyl amides.<sup>253</sup> It can be brominated in the 3 and 3' positions.<sup>199</sup>

Methyl 5-nitro- $\beta$ -resorcylic acid and sulfur chloride give the 3,3'-sulfide. Several derivatives have been made.<sup>227</sup>

### Unsymmetrical Polybasic Sulfide-Acids

Unsymmetrical acids such as  $\text{HO}_2\text{CCH}_2\text{SCMe}_2\text{CO}_2\text{H}$ ,  $\text{HO}_2\text{-CCH}_2\text{CH}_2\text{SCMe}_2\text{CO}_2\text{H}$ ,  $\text{HO}_2\text{CCHMeSCMe}_2\text{CO}_2\text{H}$ , and  $\text{HO}_2\text{-CCH}_2\text{SCH}_2\text{CHMeCO}_2\text{H}$ , can be made by the reaction of a salt of a mercapto-acid with one of a halogenated acid,<sup>149, 189d, 270b, 273c, 274, 276a, 276b, 286e</sup> or with  $\beta$ -propiolactone.<sup>172a</sup> These reactions are of the second order.<sup>54</sup>

Acids of this type are obtained by the addition of a mercapto-acid to an unsaturated acid.<sup>308</sup> Practically all that was said above about the addition of a mercapto-acid to other unsaturates applies here. Ethyl thioglycolate and ethyl cinnamate combine, in the presence of pyridine, to form the diester,  $\text{PhCH}(\text{SCH}_2\text{CO}_2\text{Et})\text{CH}_2\text{CO}_2\text{Et}$ .<sup>411</sup> The addition of methyl  $\beta$ -mercapto-propionate to methyl crotonate takes place in the presence of a quaternary base and piperidine to make the ester,  $\text{MeO}_2\text{CCH}_2\text{-CH}_2\text{SCHMeCH}_2\text{CO}_2\text{Me}$ .<sup>23</sup> Self-addition may take place with an unsaturated mercapto-acid if the mercapto group and the double bond are spaced properly, as in  $\gamma$ -mercapto- $\alpha$ -benzylideneacetoacetic ester.<sup>411</sup>

Thioglycolic,<sup>310a</sup> thiolactic,  $\beta$ -mercaptopropionic,  $\beta$ -mercapto-*i*-butyric, and  $\alpha$ -mercapto-*i*-butyric acids have all been added to maleic acid by heating the reactants, in concentrated water solution, for two hours on the steam bath and evaporating to dryness. Except with the last named, the yields are good. In this case the yield can be improved by adding sodium hydroxide to neutrality. The products are:  $\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})\text{SCH}_2\text{CO}_2\text{H}$ ,  $\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})\text{SCHMeCO}_2\text{H}$ ,  $\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})\text{-SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , and  $\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})\text{SCHMe}_2\text{CO}_2\text{H}$ .<sup>271b</sup> Thioglycolic and acrylic acids unite at pH above 7.<sup>309b, 375</sup> When thioglycolic acid and a maleic ester are brought together the addition is incomplete, but with the neutral sodium salt, in aqueous alcohol solution the union is complete. Exactly the same statements can be made about a thioglycolic ester and maleic acid.<sup>89, 312</sup> The sodium salt of thioglycolic acid unites with *N*-ethylmaleimide in water solution.<sup>294</sup> The butyl esters of the two acids unite in the presence of 1% of piperidine.<sup>363</sup> Cysteine and glutathione have each been added to maleic acid.<sup>310a</sup>

The cysteine derivative is racemized rapidly in aqueous solution.<sup>310c</sup> Thiomalic acid has been added to maleic acid.<sup>382</sup> Maleic acid inhibits enzyme reactions which are induced by mercaptans.<sup>310b</sup>

Two acids of this group have been made with chloracetic from thiomalic and thiocitromalic salts.<sup>212a</sup> Others are from mercaptoacids and  $\alpha$ -bromo derivatives of dibasic acids or esters<sup>17, 85a, 309a</sup> or from the  $\alpha$ -mercapto derivatives and chloro acid.<sup>86</sup> The acid,  $\text{HO}_2\text{CCH}_2\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , is said to inactivate metals in edible oils.<sup>129</sup>

The rotation of  $\alpha$ -( $\beta$ -naphthomercapto)propionic acid in various solvents and the rotations of the alkylmercaptosuccinic acids have been studied.<sup>295</sup>

### **bis-Sulfide-Acids**

The simplest are the disulfide-acids, such as  $\text{HO}_2\text{CCH}_2\text{S}-\text{SCH}_2\text{CO}_2\text{H}$ , but these are left to chapter 7 on disulfides.

Next come the mercaptals and mercaptoles from mercaptoacids, such as  $\text{RCH}(\text{SCH}_2\text{CO}_2\text{H})_2$  and  $\text{RR}'\text{C}(\text{SCH}_2\text{CO}_2\text{H})_2$ , which will be mentioned again in chapter 5.

Formaldehyde, acetaldehyde, furfural, cinnamic, and salicylic aldehydes, acetone, acetoacetic ester, acetophenone, benzophenone, and pyruvic and levulinic acids react readily with thioglycolic acid.<sup>48a, 48b, 55, 205b, 205c, 335a, 385</sup> A mixture of benzaldehyde with two equivalents of thioglycolic acid solidifies within a few minutes.<sup>211</sup> A number of aldehydes and ketones have been condensed with  $\beta$ -mercaptopropionic acid.<sup>209a</sup> From phenacyl bromide,  $\text{PhCOCH}_2\text{Br}$ , and thioglycolic acid a tribasic acid,  $\text{PhC}(\text{SCH}_2\text{CO}_2\text{H})_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H}$ , can be synthesized.<sup>206a</sup>  $\gamma$ -Thiobutyrolactone reacts as if it were  $\gamma$ -mercaptobutyric acid.<sup>414</sup> These acids can be made by the direct action of aldehydes and ketones on Bunte salts from haloacids.<sup>407a</sup>

In making these mercaptal and mercaptole acids it is sometimes possible to stop at the half-way stage. Thus when thiophenol and pyruvic acid are brought together, they unite with the evolution of heat. The product is the hemimercaptole,  $\text{MeC}(\text{OH})(\text{SPh})\text{CO}_2\text{H}$ . In the presence of hydrogen chloride further reaction takes place and the mercaptole,  $\text{MeC}(\text{SPh})_2\text{CO}_2\text{H}$ , is formed.<sup>128, 391d</sup> Ethyl mercaptan reacts similarly in two stages.<sup>55</sup> With phenylglyoxylic acid,  $\text{PhCOCO}_2\text{H}$ ,<sup>128</sup> and with phenylgly-

oxal<sup>391d</sup> also, the reaction can go in two steps. The reaction of thioglycolic acid with aldehydes also, may go in two steps. The hemimercaptals from thioglycolic anilide crystallize particularly well.<sup>380a</sup>

Acids of this type can be made from a dihaloacetic acid and mercaptans.<sup>46, 117</sup> When the disodium derivative of malonic ester is treated with carbon disulfide and then with methyl iodide the acid,  $(\text{MeS})_2\text{C}:\text{CHCO}_2\text{H}$ , is the final product.<sup>240, 241, 267</sup> The basic bismuth salt,  $\text{MeC}(\text{SEt})_2\text{CH}_2\text{CH}_2\text{CO}_2\text{BiO}$ , has been suggested as a therapeutic agent.<sup>90</sup>

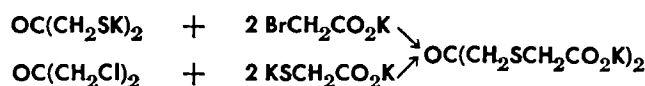
The simplest *bis*-sulfide acid, having the sulfur atoms on different carbons, is ethylene-*bis*-thioglycolic acid,  $(-\text{CH}_2\text{SCH}_2-\text{CO}_2\text{H})_2$ , which is readily made from ethylene bromide and thioglycolic acid in alkaline solution.<sup>344, 353b</sup> It forms the usual salts and can be esterified in conventional ways.<sup>422b</sup> As a *bis*-sulfide, it and its esters form complexes with platinous,<sup>344, 422b</sup> cuprous, and cupric chlorides<sup>422b</sup> and with silver nitrate.<sup>344, 422b</sup> The acid has been oxidised to the *bis*-sulfoxide and *bis*-sulfone.<sup>422b</sup>

Ethylene mercaptan reacts well with alpha and beta halopropionic acids.<sup>353b, 353c</sup> It should react equally well with other haloacids but this has not been exploited. The isothiuronium salts, from which the dimercaptans  $\text{HS}(\text{CH}_2)_n\text{SH}$  are prepared, can be used directly with chloroacetic acid and other haloacids.<sup>249</sup> Ethylene mercaptan is unusually active in addition reactions.<sup>268</sup> It can be added to unsaturated acids or to their nitriles.

The acid,  $\text{CH}_2(\text{CH}_2\text{SCH}_2\text{CO}_2\text{H})_2$ , from trimethylene bromide and thioglycolic acid, has been reported. A number of its derivatives have been made.<sup>360</sup>

From thioglycolic acid and the bromides,  $\text{Br}(\text{CH}_2)_n\text{Br}$ , a series of acids,  $\text{HO}_2\text{CCH}_2\text{S}(\text{CH}_2)_n\text{SCH}_2\text{CO}_2\text{H}$ , in which  $n$  varies from 1 to 6, has been prepared and oxidised to the *bis*-sulfoxides.<sup>270a</sup> The primary and secondary dissociation constants have been determined.<sup>2</sup> From  $\beta$ -mercaptopropionic acid, three acids,  $\text{HO}_2\text{CCH}_2\text{CH}_2\text{S}(\text{CH}_2)_n\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , in which  $n = 3, 4$ , and  $5$ , have been prepared.<sup>275</sup>

The acid,  $\text{O}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , from dichloroethyl ether has been described.<sup>168</sup> The keto-acid,  $\text{OC}(\text{CH}_2\text{SCH}_2-\text{CO}_2\text{H})_2$ , has been made in two ways:<sup>378a</sup>



The unsymmetrical acid,  $\text{HO}_2\text{CCH}_2\text{SCHMeCH}_2\text{SCH}_2\text{CO}_2\text{H}$ , is from propylene dimercaptan.<sup>353a</sup> The acid,  $(\text{MeSCH}_2)_2\text{CHCO}_2\text{H}$ , has been made from the dimercapto-acid,  $(\text{HSCH}_2)_2\text{CHCO}_2\text{H}$ , and methyl iodide.<sup>229</sup> The ester,  $\text{EtO}_2\text{CCH}_2\text{SCHPh}\cdot\text{CH}_2\text{SCH}_2\text{CO}_2\text{Et}$ , is the addition product of styrene and ethyl dithiodiglycolate,  $(\cdot\text{SCH}_2\text{CO}_2\text{Et})_2$ .<sup>207b</sup>

Methanesulfonyl chloride and acetoacetic ester give the  $\alpha$ -methylmercapto- and  $\alpha,\alpha'$ -bis-methylmercapto-acetoacetic esters,  $\text{MeCOCH}(\text{SMe})\text{CH}_2\text{CO}_2\text{Et}$  and  $\text{MeCOC}(\text{SMe})_2\text{CO}_2\text{Et}$ .<sup>56</sup>

6,8-bis-Benzylmercapto-octioic acid has been made in two ways.<sup>349, 393</sup> Debenzylating this is one way to make lipoic acid.

### Selenide-Acids

A few of these are known. The selenodilactic acid, DL-Se- $(\text{CHMeCO}_2\text{H})_2$ , has been resolved into the two active acids.<sup>146a, 147b</sup> Selenodiacetic,  $\beta$ -selenodipropionic,<sup>325</sup> and  $\gamma$ -selenodibutyric<sup>147b, 148</sup> acids have been prepared by the methods used for the sulfur analogs. By adding selenium to the Grignard reagent and causing the product to react with chloroacetic acid the acid  $m\text{-CF}_3\text{C}_6\text{H}_4\text{SeCH}_2\text{COOH}$  has been made.<sup>33</sup> Phenylselenoacetic acid,  $\text{PhSeCH}_2\text{CO}_2\text{H}$ , has been made by the pyrolysis of the selenonium salt,  $\text{PhMeSe}(\text{CH}_2\text{CO}_2\text{H})\text{Br}$ .<sup>122</sup> The nitro derivative of this was obtained by heating *o*-nitrophenyl selenocyanide,  $o\text{-O}_2\text{NC}_6\text{H}_4\text{SeCN}$ , with sodium chloroacetate.<sup>30</sup> *p*-Phenyl-selenobenzoic acid,  $\text{PhSeC}_6\text{H}_4\text{CO}_2\text{H}$ , was from the reduction of the selenoxide.<sup>158</sup> The affinity constants of the acids,  $\text{AmOCH}_2\text{CO}_2\text{H}$ ,  $\text{AmSCH}_2\text{CO}_2\text{H}$ , and  $\text{AmSeCH}_2\text{CO}_2\text{H}$ , have been compared.<sup>30</sup>

### Physical Properties of Some Sulfide-Acids

These are given in the following lists. The same remarks that have been made in other chapters apply here.

#### Alkylmercaptoacetic Acids

$\text{MeSCH}_2\text{CO}_2\text{H}$ , m.  $13^\circ$ ;  $b_4$   $99\text{--}100^\circ$ ,<sup>326</sup>  $b_8$   $106\text{--}8^\circ$ ,<sup>206b</sup>  $b_{9.5}$   $107^\circ$ ,<sup>297a</sup>  $b_{27}$   $130\text{--}1^\circ$ ; d  $20/4$  1.221; n  $20/D$  1.495;  $K_{25}$   $1.92 \times 10^{-4}$ ; <sup>273b</sup>, <sup>297a</sup> K esterification 3.80 at  $25^\circ$ ; <sup>326</sup> chloride,  $b_{14}$   $49\text{--}50^\circ$ ; <sup>305, 307</sup> n  $25/D$  1.4967; anhydride,  $b_{0.25}$   $111\text{--}2^\circ$ ; n  $25/D$  1.5162; <sup>305</sup> Me ester,  $b_{11}$   $53\text{--}5^\circ$ ,  $b_{20}$   $60\text{--}2^\circ$ ; <sup>247</sup> Et ester, b.  $174\text{--}6^\circ$ ; amide, b.  $104^\circ$ ; <sup>246</sup> anilide, m.  $78^\circ$ ,<sup>187</sup>  $74^\circ$ ; <sup>28b</sup> *p*-toluide, m.  $103^\circ$ ; <sup>187</sup> *p*-aniside, m.  $94^\circ$ ; *p*-phenetide, m.  $63^\circ$ .<sup>28d</sup>

- EtSCH<sub>2</sub>CO<sub>2</sub>H, m. -8.5°;<sup>326</sup> -8.7°; <sup>342c</sup> b<sub>5</sub> 108-9°; <sup>326</sup> b<sub>11</sub> 117-8°; <sup>43</sup>, <sup>342c</sup> b<sub>14</sub> 124-5°; <sup>206b</sup> n 20/D 1.4869; <sup>297a</sup> d 20/4 1.1497; <sup>342c</sup> K  $1.83 \times 10^{-4}$ ; <sup>297a</sup>, <sup>342c</sup> K esterification 3.83 at 25°; <sup>326</sup> chloride, b<sub>14</sub> 61-4°; <sup>305</sup>, <sup>307</sup> n 25/D 1.4888; <sup>305</sup> anhydride, b<sub>0.07</sub> 94-6°; <sup>307</sup> 94°, b<sub>0.1</sub> 100-3°; n 25/D 1.5030; <sup>305</sup> Et ester, b. 187-9°; <sup>250a</sup>, <sup>250b</sup> d<sub>4</sub> 1.047; <sup>250b</sup> amide, m. 51°; <sup>334b</sup> 44°; <sup>250a</sup>, <sup>250b</sup> anilide, m. 59°; <sup>187</sup> 61°; <sup>28a</sup> *p*-toluide, m. 82°; <sup>187</sup> *p*-aniside, m. 68°, *p*-phenetide, m. 87°; <sup>28d</sup> Et thioester b<sub>5</sub> 101-2°.<sup>341</sup>
- PrSCH<sub>2</sub>CO<sub>2</sub>H, b<sub>685</sub> 244-5°; <sup>298</sup> b<sub>8.5</sub> 125-6°; <sup>206b</sup> b<sub>11</sub> 126-8°; <sup>305</sup>, <sup>307</sup> b<sub>15</sub> 132°; d 20/4 1.106; n 20/D 1.483; <sup>273b</sup> n 25/D 1.4805; <sup>305</sup> K  $1.68 \times 10^{-4}$ ; <sup>273b</sup> chloride, b<sub>8</sub> 63-4°; <sup>305</sup>, <sup>307</sup> n 25/D 1.4846; <sup>305</sup> Me ester, b. 184°; d 25/4 1.0325; n 25/D 1.4630; Et ester, b. 205°; d 25/4 0.9913; n 25/D 1.4590; Pr ester, b. 209°; d 25/4 0.9860; n 25/D 1.4580; Bu ester, b. 225°; d 25/4 0.9781; n 25/D 1.4575; amide, m. 53°; <sup>425</sup> anilide, m. 57°; <sup>28b</sup> 56°; *p*-toluide, m. 79°.<sup>187</sup>
- i*-PrSCH<sub>2</sub>CO<sub>2</sub>H, b<sub>10</sub> 123-4°; <sup>206b</sup> b<sub>13</sub> 128°; <sup>273b</sup> b<sub>10</sub> 118-9°; n 25/D 1.4788; <sup>305</sup>, <sup>307</sup> K  $1.9 \times 10^{-4}$  at 25°; <sup>273b</sup> chloride, b<sub>8</sub> 57-8°; <sup>305</sup>, <sup>307</sup> n 25/D 1.4820; <sup>305</sup> anilide, m. 67°; <sup>28b</sup>, <sup>187</sup> *p*-toluide, m. 66°; <sup>187</sup> *p*-aniside, m. 58°; *p*-phenetide, m. 100°.<sup>28d</sup>
- BuSCH<sub>2</sub>CO<sub>2</sub>H, b<sub>764</sub> 282.2°; <sup>427</sup> b<sub>20</sub> 153°; <sup>273b</sup> b<sub>10</sub> 136-7°; <sup>305</sup>, <sup>307</sup> b<sub>5-6</sub> 125-30°; <sup>334a</sup> d 0/4 1.0769, d 25/4 1.0600; <sup>427</sup> n 25/D 1.4780; <sup>305</sup> K  $1.54 \times 10^{-4}$ ; <sup>273b</sup> chloride, b. 218°; <sup>427</sup> b<sub>8</sub> 83-4°; <sup>305</sup>, <sup>307</sup> n 25/D 1.4828; <sup>305</sup> Me ester, b. 224°, b<sub>10</sub> 85°; d 0/4 1.0297, d 25/4 1.0096; n 25/D 1.4590; Et ester, b. 235.5°, b<sub>10</sub> 89-90°; <sup>427</sup> b<sub>18</sub> 110-1°; <sup>133a</sup> d 0/4 1.0042, d 25/4 0.9852; n 25/D 1.4560; Pr ester, b. 250.2°, b<sub>6</sub> 93-4°; d 0/4 0.9890, d 25/4 0.9694; n 25/D 1.4555; Bu ester, b. 263.8°, b<sub>8</sub> 105-6°; d 0/4 0.9792, d 25/4 0.9601; n 25/D 1.4555; <sup>427</sup> amide, m. 58°; <sup>117</sup> 65°; <sup>427</sup> *p*-toluide, m. 62°.<sup>187</sup>
- i*-BuSCH<sub>2</sub>CO<sub>2</sub>H, b. 244°; <sup>352</sup>, <sup>426</sup> b<sub>2.5</sub> 108°; <sup>12</sup> d<sub>25</sub> 1.0685; n 25/D 1.4750; chloride, b<sub>14</sub> 104-5°; d<sub>25</sub> 1.1034; n 25/D 1.4780; Et ester, b. 209°; d 25/4 0.9819; n 25/D 1.4550; Pr ester, b. 228°; d 25/4 0.9619; n 25/D 1.4550; Bu ester, b. 245°; d 25/4 0.9548; n 25/D 1.4515; *i*-Bu ester, b. 234°; d 25/4 0.9498; n 25/D 1.4530; <sup>352</sup>, <sup>426</sup> amide, m. 49°; <sup>426</sup> 58°; <sup>117</sup> anilide, m. 46°; *p*-toluide, m. 86°; <sup>187</sup> *p*-aniside, m. 86°.<sup>28d</sup>
- s*-BuSCH<sub>2</sub>CO<sub>2</sub>H, b<sub>5</sub> 118-20°; <sup>394</sup> *p*-toluide, m. 57°.<sup>187</sup>
- t*-BuSCH<sub>2</sub>CO<sub>2</sub>H, b<sub>2</sub> 107-9°; <sup>187</sup> b<sub>8</sub> 126-7°; <sup>206b</sup> chloride, b<sub>8</sub> 68-70°; anilide, m. 81°; *p*-toluide, m. 88°.<sup>187</sup>

- AmSCH<sub>2</sub>CO<sub>2</sub>H, m. 20.5°; <sup>234</sup> b<sub>0.75</sub> 107.5–9°; <sup>394</sup> b<sub>0.5</sub> 120–2°; d 20/4 1.0425; n 20/D 1.4781; <sup>234</sup> n 25/D 1.4723. <sup>394</sup>
- i*-AmSCH<sub>2</sub>CO<sub>2</sub>H, b<sub>0.75</sub> 103–6°; n 25/D 1.4748; <sup>394</sup> Et ester, b. 230°; d<sub>4</sub> 0.9797. <sup>250a, 250b</sup>
- C<sub>6</sub>H<sub>13</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>2</sub> 133–6°; n 25/D 1.4723. <sup>394</sup>
- Pr<sub>2</sub>CHSCH<sub>2</sub>CO<sub>2</sub>H, b<sub>1</sub> 124–6°. <sup>394</sup>
- Me<sub>2</sub>CHCH<sub>2</sub>CHMeCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>1</sub> 112–6°; n 25/D 1.4734. <sup>394</sup>
- C<sub>8</sub>H<sub>17</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 37°; <sup>345</sup> 35°; <sup>157</sup> b<sub>2</sub> 150–4°; <sup>169, 345</sup> b<sub>5</sub> 175–7°. <sup>394</sup>
- 2-Octyl SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>0.7</sub> 130–1°. <sup>394</sup>
- 4-Octyl SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>0.75</sub> 120–2°; n 25/D 1.4789. <sup>394</sup>
- C<sub>10</sub>H<sub>21</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 53°; <sup>169, 345</sup> b<sub>4</sub> 150–60°. <sup>348</sup>
- C<sub>12</sub>H<sub>25</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 62°; <sup>169, 345</sup> b<sub>2</sub> 176–9°. <sup>190c</sup>
- C<sub>14</sub>H<sub>29</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 61°. <sup>394</sup>
- C<sub>16</sub>H<sub>33</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 74°. <sup>196</sup>
- C<sub>6</sub>H<sub>11</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>0.1</sub> 122°; <sup>100</sup> b<sub>12</sub> 173–8°; <sup>190c</sup> d<sub>20</sub> 1.1274; n 20/D 1.5142. <sup>437a</sup>
- 2-MeC<sub>6</sub>H<sub>10</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>0.1</sub> 135°. <sup>100</sup>
- C<sub>10</sub>H<sub>17</sub>SC<sub>2</sub>CO<sub>2</sub>H, decahydronaphthyl, b<sub>2</sub> 170–2°. <sup>190c</sup>
- 2-C<sub>4</sub>H<sub>9</sub>S·SCH<sub>2</sub>CO<sub>2</sub>H, Et ester, b<sub>20</sub> 138°; amide, m. 96°. <sup>81</sup>
- 3-C<sub>4</sub>H<sub>9</sub>S·SCH<sub>2</sub>CO<sub>2</sub>H, m. 52.5°; <sup>59</sup> 51°; <sup>81</sup> 56°; <sup>300</sup> b<sub>1</sub> 135–40°; <sup>394</sup> Et ester, b<sub>9</sub> 140–2°; amide, m. 116°; acetanilide, m. 118.5°. <sup>81</sup>
- 2-C<sub>4</sub>H<sub>9</sub>S·CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>16</sub> 196.5°; d 22/4 1.319; n 20/D 1.5898; Et ester, b<sub>15.5</sub> 160°; d 20.5/4 1.192; n 20/D 1.5452; chloride, b<sub>16</sub> 150°; amide, m. 102.5°. <sup>73</sup>

### Arylmercaptoacetic Acids

- PhSCH<sub>2</sub>CO<sub>2</sub>H, m. 65°; <sup>206b</sup> 43.5°; <sup>250a</sup> K  $3.0 \times 10^{-4}$ ,  $2.8 \times 10^{-4}$  at 25°; <sup>96</sup> chloride b<sub>8</sub> 117–9°; n 25/D 1.5806; <sup>305</sup> Et ester, b. 276–8°; <sup>250b</sup> b<sub>14</sub> 144–5°; <sup>340b</sup> lauryl ester, b<sub>15</sub> 244–6°; <sup>193</sup> amide, m. 104°. <sup>250b</sup>
- PhSCH<sub>2</sub>COSPh, m. 65°. <sup>104</sup>
- PhCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 64°; <sup>273b</sup> 63°; <sup>205d, 206b</sup> 62°; <sup>157</sup> 61°; <sup>192, 407b</sup> 59°; <sup>154a, 415</sup> b<sub>20</sub> 204°; K  $1.87 \times 10^{-4}$ ; <sup>273b</sup> Et ester, b. 275–90°; <sup>154a</sup> chloride, b<sub>5.5</sub> 130°; n 25/D 1.5682; <sup>305</sup> amide, m. 97°; <sup>154a</sup> *p*-aniside, m. 82°; *p*-phenetide, m. 111°; <sup>28d</sup> thioamide, m. 78.5°. <sup>102</sup>
- PhCHMeSCH<sub>2</sub>CO<sub>2</sub>H, m. 63°; <sup>206b, 206c</sup> L form  $[\alpha]_D -333.2^\circ$ . <sup>207a</sup>
- PhCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 61°; <sup>53</sup> 56°; <sup>394</sup> b<sub>4</sub> 185°; <sup>53</sup> b<sub>2</sub> 194–5°; Me ester, b<sub>4</sub> 146°; <sup>394</sup> chloride, b<sub>15</sub> 175–6°. <sup>53</sup>



- PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>0.6</sub> 187–8°;<sup>53</sup> *b*<sub>1</sub> 173–5°; Me ester, *b*<sub>3</sub> 152°;<sup>394</sup> chloride, *b*<sub>13</sub> 193–5°.<sup>53</sup>
- m*-MeC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 68°.<sup>417</sup>
- p*-MeC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 86°; Et ester, *b*<sub>32</sub> 179–82°; *n* 22.5/D 1.5058.<sup>394</sup>
- p*-ClC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 62°.<sup>315</sup>
- 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 123°.<sup>232</sup>
- 2,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 130°.<sup>159</sup>
- 4,2-ClMeC<sub>6</sub>H<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 128°;<sup>232</sup> 127°.<sup>438</sup>
- p*-BrC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>5</sub> 175°.<sup>394</sup>
- m*-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 47°; *b*<sub>2</sub> 140–3°; Me ester, *b*<sub>1</sub> 100–1°.<sup>394</sup>
- 2,4-O<sub>2</sub>NCIC<sub>6</sub>H<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 210°.<sup>356</sup>
- 2,6,4-I<sub>2</sub>O<sub>2</sub>NC<sub>6</sub>H<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 112°.<sup>410</sup>
- o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 164°; Et ester, m. 48°.<sup>91</sup>
- 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 160°.<sup>91</sup>
- p*-HSC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 111°.<sup>394</sup>
- p*-MeOC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>Me, *b*<sub>5</sub> 162°.<sup>394</sup>
- p*-PhOC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 74°; Me ester, *b*<sub>1.8</sub> 197–200°.<sup>394</sup>
- 5,2-Me(MeO)C<sub>6</sub>H<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 79°.<sup>163</sup>
- Ph<sub>2</sub>CHSCH<sub>2</sub>CO<sub>2</sub>H, m. 127°;<sup>157</sup> amide, m. 112°; Et ester, *b*<sub>0.001</sub> 125°.<sup>103</sup>
- Ph<sub>3</sub>CSCH<sub>2</sub>CO<sub>2</sub>H, m. 164°;<sup>205a</sup> 163°;<sup>192</sup> 162°; *K* 0.5 × 10<sup>-4</sup>; 273b Et ester, m. 94°; amide, m. 146°.<sup>102</sup>
- p*-Me<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>0.15</sub> 160–80°.<sup>394</sup>
- 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 97°.<sup>394</sup>
- p*-PhC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 170°.<sup>155</sup>
- α-C<sub>10</sub>H<sub>7</sub>SCH<sub>2</sub>CO<sub>2</sub>Me, *b*<sub>1.5</sub> 195–8°.<sup>394</sup>
- β-C<sub>10</sub>H<sub>7</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 150°;<sup>157</sup> 77°; Et ester, *b*<sub>0.2</sub> 148–50°.<sup>394</sup>
- α-C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 104°.<sup>192</sup>
- 9-C<sub>14</sub>H<sub>9</sub>SCH<sub>2</sub>CO<sub>2</sub>H, anthranyl, m. 164°; Me ester, m. 57°.<sup>151</sup>
- p*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 64°;<sup>394</sup> 48°.<sup>192</sup>
- 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 75°.<sup>315</sup>
- 2-benzothiazoyl-SCH<sub>2</sub>CO<sub>2</sub>H, m. 155°;<sup>120</sup> Bu ester, *b*<sub>1</sub> 200–8°.<sup>107</sup>

### Unsaturated Alkyl- and Arylmercaptoacetic Acids

- MeCH:CEtSCH<sub>2</sub>CO<sub>2</sub>Et, *b*<sub>2</sub> 78.5°; *d* 20/4 1.0109; *n* 20/D 1.4797.<sup>385</sup>
- EtCH:CPrSCH<sub>2</sub>CO<sub>2</sub>Et, *b*<sub>1.8</sub> 90°; *d* 20/4 0.9820; *n* 20/D 1.4749.<sup>385</sup>

PrCH:CBuSCH<sub>2</sub>CO<sub>2</sub>Et, *b*<sub>1.8</sub> 108°; *d* 20/4 0.9570; *n* 20/D 1.4750.<sup>385</sup>

PhCH:CHSCH<sub>2</sub>CO<sub>2</sub>H, *m.* 90°; *K* 3.1 × 10<sup>-4</sup>.<sup>210</sup>

H<sub>2</sub>C:CHCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>1.5</sub> 103-5°;<sup>394</sup> *b*<sub>0.8</sub> 100-12°;<sup>12</sup> *n* 25/D 1.5045; Et ester, *b*<sub>1</sub> 64-7°;<sup>394</sup> *p*-phenetide, *m.* 78°.<sup>28d</sup>

H<sub>2</sub>C:CMeCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>3.4</sub> 114-8°; *n* 25/D 1.4993.<sup>394</sup>

Me<sub>2</sub>C:CHCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>0.5</sub> 103-6°; *n* 25/D 1.5058.<sup>394</sup>

H<sub>2</sub>C:CClCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>1</sub> 130-1°; *n* 24/D 1.5336.<sup>394</sup>

H<sub>2</sub>C:CB<sub>r</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *m.* 30.5°; *b*<sub>1.5</sub> 145-8°; *n* 25/D 1.5530.<sup>394</sup>

MeCCl:CHCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>0.6</sub> 108-11°.<sup>142</sup>

PhCH:CHCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *m.* 90°;<sup>209c</sup> Et ester, *m.* 79°;<sup>205d</sup> 72°.<sup>394</sup>

Me<sub>2</sub>C:CHCH<sub>2</sub>CH<sub>2</sub>(CHMe)<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, *b*<sub>0.1</sub> 170°.<sup>100</sup>

### Alkylmercapto Monocarboxylic Acids

MeSCHMeCO<sub>2</sub>H, *m.* 17.3°;<sup>297b</sup> *b*<sub>12</sub> 112-15°;<sup>307</sup> *b*<sub>8</sub> 104°;<sup>297a</sup> 105-6°;<sup>305</sup> *b*<sub>4</sub> 105-6°; *d* 20/4 1.1464;<sup>297b</sup> *n* 20/D 1.4843;<sup>297a, 297b</sup> *n* 25/D 1.4815;<sup>305</sup> *K* 1.73 × 10<sup>-4</sup>; <sup>297a</sup> chloride, *b*<sub>10</sub> 48-50°;<sup>307</sup> *b*<sub>45</sub> 77-8°; *n* 25/D 1.4873;<sup>305</sup> anilide, *m.* 126°.<sup>28b</sup>

EtSCHMeCO<sub>2</sub>H, *b*<sub>8</sub> 113.7°;<sup>297a</sup> 111-3°;<sup>305, 307</sup> *b*<sub>9</sub> 115.5°; *d* 20/4 1.1087;<sup>297b</sup> *n* 20/D 1.4796;<sup>297a</sup> 1.4798;<sup>297b</sup> *n* 25/D 1.4764;<sup>305</sup> *K* 1.60 × 10<sup>-4</sup>; <sup>297a</sup> chloride, *b*<sub>8</sub> 56-7°;<sup>305, 307</sup> *n* 25/D 1.4805;<sup>305</sup> amide, *m.* 65.5°;<sup>334b</sup> anilide, *m.* 97°.<sup>28a</sup>

PrSCHMeCO<sub>2</sub>H, *b*<sub>9</sub> 128.5°; *d* 20/4 1.0595; *n* 20/D 1.4765;<sup>297b</sup> amide, *m.* 57°;<sup>334b</sup> anilide, *m.* 92°.<sup>28b</sup>

*i*-PrSCHMeCO<sub>2</sub>H, *m.* 14.6°; *b*<sub>9</sub> 121.4°; *d* 20/4 1.0482; *n* 20/D 1.4724;<sup>297b</sup> anilide, *m.* 84°.<sup>28b</sup>

BuSCHMeCONH<sub>2</sub>, *m.* 61.5°.<sup>334b</sup>

*t*-BuSCHMeCO<sub>2</sub>H, *m.* 92°.<sup>16</sup>

C<sub>16</sub>H<sub>33</sub>SCHMeCO<sub>2</sub>H, *m.* 59°.<sup>196</sup>

MeSCHEtCO<sub>2</sub>H, *b*<sub>1</sub> 90-1°;<sup>62</sup> *b*<sub>8</sub> 115-6°;<sup>305</sup> *b*<sub>9</sub> 115-6°;<sup>307</sup> *n* 25/D 1.4788;<sup>305</sup> chloride, *b*<sub>8</sub> 58-9°;<sup>305, 307</sup> *n* 25/D 1.4835;<sup>305</sup> amide, *m.* 99°;<sup>62</sup> anilide, *m.* 112°;<sup>28b</sup> *p*-toluide, *m.* 89°.<sup>28e</sup>

EtSCHEtCONH<sub>2</sub>, *m.* 101°;<sup>334b</sup> anilide, *m.* 68°;<sup>28a</sup> *p*-toluide, *m.* 70°.<sup>28e</sup>

PrSCHEtCONH<sub>2</sub>, *m.* 78.5°;<sup>334b</sup> *p*-toluide, *m.* 69°.<sup>28e</sup>

*i*-PrSCHEtCONHPh, *m.* 88°;<sup>28b</sup> *p*-toluide, *m.* 118°.<sup>28e</sup>

BuSCHEtCONH<sub>2</sub>, *m.* 65.5°.<sup>334b</sup>

C<sub>14</sub>H<sub>29</sub>SCHEtCO<sub>2</sub>H, *m.* 39°.<sup>196</sup>

- $\text{EtSCHPrCONH}_2$ , m.  $102^\circ$ .<sup>334b</sup>  
 $\text{PrSCHPrCONH}_2$ , m.  $99^\circ$ .<sup>334b</sup>  
 $\text{BuSCHPrCONH}_2$ , m.  $65^\circ$ .<sup>334b</sup>  
 $\text{C}_{16}\text{H}_{33}\text{SCHPrCO}_2\text{H}$ , m.  $49^\circ$ .<sup>196</sup>  
 $\text{C}_{16}\text{H}_{33}\text{SCHBuCO}_2\text{H}$ , m.  $49.5^\circ$ .<sup>196</sup>  
 $\text{C}_{16}\text{H}_{33}\text{SCH}(\text{C}_8\text{H}_{17})\text{CO}_2\text{H}$ , m.  $43^\circ$ .<sup>196</sup>  
 $\text{C}_{12}\text{H}_{25}\text{SCH}(\text{C}_9\text{H}_{19})\text{CO}_2\text{H}$ , m.  $48^\circ$ .<sup>196</sup>  
 $\text{C}_{16}\text{H}_{33}\text{SCH}(\text{C}_9\text{H}_{19})\text{CO}_2\text{H}$ , m.  $49^\circ$ .<sup>196</sup>  
 $\text{C}_{16}\text{H}_{33}\text{SCH}(\text{C}_{10}\text{H}_{21})\text{CO}_2\text{H}$ , m.  $48^\circ$ .<sup>196</sup>  
 $\text{C}_{16}\text{H}_{33}\text{SCH}(\text{C}_{12}\text{H}_{25})\text{CO}_2\text{H}$ , m.  $48^\circ$ .<sup>196</sup>  
 $\text{C}_{16}\text{H}_{33}\text{SCH}(\text{C}_{14}\text{H}_{29})\text{CO}_2\text{H}$ , m.  $48^\circ$ .<sup>196</sup>  
 $\text{MeSCMe}_2\text{CO}_2\text{H}$ , m.  $40$ ;  $b_{12}$   $113-5^\circ$ .<sup>277</sup>  
 $\text{EtSCMe}_2\text{CO}_2\text{H}$ ,  $b_{20}$   $132-3^\circ$ ;  $d$   $20/4$   $1.0604$ ;  $n$   $20/D$   $1.4764$ ; <sup>277</sup>  
 amide, m.  $94^\circ$ .<sup>334b</sup>  
 $\text{PrSCMe}_2\text{CONH}_2$ , m.  $95.5^\circ$ .<sup>334b</sup>  
 $i\text{-PrSCMe}_2\text{CO}_2\text{H}$ , m.  $43^\circ$ ;  $b_{15}$   $131-2^\circ$ .<sup>277</sup>  
 $\text{BuSCMe}_2\text{CONH}_2$ , m.  $108^\circ$ .<sup>334b</sup>  
 $\text{MeSCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $16.5^\circ$ ;  $b_7$   $129.5^\circ$ ,<sup>326</sup>  $b_{12}$   $119-23^\circ$ ,<sup>305, 307</sup>  $b_{14}$   
 $129.5^\circ$ ;  $d$   $20/4$   $1.1571$ ;  $n$   $20/D$   $1.4898$ ,<sup>215</sup>  $n$   $25/D$   $1.4884$ ; <sup>305</sup>  
 $\text{K}$  esterification  $4.60$  at  $25^\circ$ ; <sup>326</sup> chloride,  $b_{12}$   $65-7^\circ$ ,<sup>307</sup>  $b_{45}$   $96-$   
 $7^\circ$ ,<sup>305</sup>  $b_{34}$   $98-101^\circ$ ;  $n$   $20/D$   $1.500$ ,<sup>215</sup>  $n$   $25/D$   $1.4941$ ; <sup>305</sup>  $\text{Me}$  ester,  
 $b_4$   $77-8^\circ$ ,<sup>413</sup>  $b_{11}$   $69^\circ$ ,<sup>177</sup>  $b_{15}$   $80.5^\circ$ ;  $d$   $20/4$   $1.073$ ;  $n$   $20/D$   $1.4646$ ,<sup>215</sup>  
 $n$   $32/D$   $1.4600$ ;  $\text{Et}$  ester,  $b_{18}$   $88^\circ$ .<sup>413</sup>  
 $\text{EtSCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $23.5^\circ$ ;  $b_5$   $131.5^\circ$ ,<sup>326</sup>  $b_{13}$   $136-7^\circ$ ,<sup>272a</sup>  $b_{20}$   
 $149^\circ$ ;  $d$   $25/4$   $1.103$ ;  $n$   $25/D$   $1.4756$ ; <sup>112</sup>  $\text{K}$  esterification  $4.64$  at  
 $25^\circ$ ; <sup>326</sup>  $\text{Me}$  ester,  $b_{55}$   $109-13^\circ$ ,<sup>33</sup>  $b_{14}$   $84^\circ$ ,<sup>243</sup>  $b_{11}$   $73^\circ$ ; <sup>84</sup>  $n$   $20/D$   
 $1.4630$ ; <sup>243</sup>  $\text{Et}$  ester,  $b_{18}$   $95-7^\circ$ .<sup>413</sup>  
 $\text{PrSCH}_2\text{CH}_2\text{CO}_2\text{H}$ ,  $b_{10}$   $142-3^\circ$ ,<sup>272a</sup>  $b_{11}$   $142-5^\circ$ ; <sup>406</sup>  $\text{Me}$  ester,  $b_4$   
 $63^\circ$ ;  $n$   $21/D$   $1.4629$ .<sup>243</sup>  
 $i\text{-PrSCH}_2\text{CH}_2\text{CO}_2\text{Me}$ ,  $b_{13}$   $94^\circ$ ;  $d$   $20/4$   $1.010$ ;  $n$   $20/D$   $1.4610$ .<sup>215</sup>  
 $\text{BuSCH}_2\text{CH}_2\text{CO}_2\text{H}$ ,  $b_{20}$   $168-9^\circ$ ;  $d$   $25/4$   $1.043$ ;  $n$   $25/D$   $1.4706$ ; <sup>112</sup>  
 $\text{Me}$  ester,  $b_{19}$   $118^\circ$ .<sup>133a</sup>  
 $t\text{-BuSCH}_2\text{CH}_2\text{CO}_2\text{H}$ ,  $b_1$   $98-9^\circ$ ; <sup>169, 172a</sup>  $\text{Me}$  ester,  $b_{17}$   $102^\circ$ ;  $d$   $20/4$   
 $0.984$ ;  $n$   $20/D$   $1.4604$ .<sup>215</sup>  
 $\text{C}_6\text{H}_{13}\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $21.5^\circ$ ; <sup>169</sup>  $b_1$   $110-4^\circ$ .<sup>169, 172a</sup>  
 $\text{C}_8\text{H}_{17}\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $41^\circ$ .<sup>169, 345</sup>  
 $\text{C}_9\text{H}_{19}\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $53^\circ$ ,<sup>345</sup>  $51^\circ$ ; <sup>169</sup>  $b_{25}$   $180-5^\circ$ .<sup>345</sup>  
 $\text{C}_{10}\text{H}_{21}\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $52^\circ$ ,<sup>169</sup>  $43^\circ$ .<sup>384</sup>  
 $\text{C}_{12}\text{H}_{25}\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $62^\circ$ ,<sup>169, 243, 345</sup>  $60^\circ$ .<sup>384</sup>

- $C_{18}H_{37}SCH_2CH_2CO_2H$ , m.  $79^\circ$ .<sup>384</sup>  
 $C_6H_{11}SCH_2CH_2CO_2H$ , m.  $22^\circ$ ;  $b_{0.9}$   $136-7^\circ$ ; n 20/D 1.5096;  $d_{20}$  1.1000.<sup>437a</sup>  
 $2-C_4H_9S \cdot CH_2SCH_2CH_2CO_2H$ , m.  $70.5^\circ$ ;  $b_{18}$   $204^\circ$ ; chloride,  $b_{15}$   $175^\circ$ ; amide, m.  $94^\circ$ .<sup>73</sup>  
 $MeSCHMeCH_2CO_2H$ ,  $b_1$   $98-100$ ; amide, m.  $80^\circ$ .<sup>62</sup>  
 $EtSCHMeCH_2CO_2Me$ ,  $b_{10}$   $79^\circ$ .<sup>84</sup>  
 $MeSCH_2CHMeCO_2H$ ,  $b_{12}$   $129-30^\circ$ ; d 20/4 1.1086; n 20/D 1.4815; <sup>271a</sup> Me ester,  $b_{12}$   $79^\circ$ ; d 20/4 1.037; n 20/D 1.4610.<sup>215</sup>  
 $EtSCH_2CHMeCO_2H$ ,  $b_{12}$   $140-1^\circ$ ; d 20/4 1.0684; n 20/D 1.4780.<sup>271a</sup>  
 $PrSCH_2CHMeCO_2H$ ,  $b_6$   $138-9^\circ$ ; d20/4 1.0405; n 20/D 1.4761.<sup>271a</sup> n 20/D 1.4761.<sup>271a</sup>  
*i*- $PrSCH_2CHMeCO_2H$ , m.  $31^\circ$ ;  $b_8$   $135-7^\circ$ ; <sup>271a</sup> Me ester,  $b_{10}$   $91^\circ$ ; d 20/4 0.986; n 20/D 1.4578.<sup>215</sup>  
 $BuSCH_2CHMeCONH_2$ , m.  $55^\circ$ .<sup>334b</sup>  
 $MeSCHEtCH_2CO_2H$ ,  $b_1$   $90-1^\circ$ ; amide, m.  $99^\circ$ .<sup>62</sup>  
 $EtSCH_2CHEtCO_2H$ ,  $b_{18}$   $137^\circ$ .<sup>45</sup>  
 $MeSCH_2CH(CH_2Ph)CO_2H$ , m.  $104^\circ$ ;  $b_{13}$   $181-6^\circ$ .<sup>45</sup>  
 $C_{12}H_{25}SCMe_2CH_2CO_2Me$ ,  $b_{0.5}$   $162-3.5^\circ$ ; n 20/D 1.4660.<sup>404</sup>  
 $MeSCH_2CH_2CH_2CO_2H$ ,  $b_5$   $127-9^\circ$ ,<sup>254</sup>, <sup>332</sup>  $b_7$   $123^\circ$ ,<sup>418</sup>  $b_9$   $129-30^\circ$ ,<sup>307</sup>  $130^\circ$ ,<sup>305</sup>  $b_{12}$   $130-3^\circ$ ,<sup>24</sup>  $b_{18}$   $143-4^\circ$ ; <sup>311</sup> n 25/D 1.4823; <sup>305</sup> chloride,  $b_7$   $77-9^\circ$ ,<sup>307</sup>  $b_{20}$   $98-100^\circ$ ; n 25/D 1.4898.<sup>305</sup>  
 $EtSCH_2CH_2CH_2CO_2H$ ,  $b_{10}$   $144^\circ$ ,<sup>15</sup>  $b_{20}$   $155^\circ$ .<sup>418</sup>  
 $PrSCH_2CH_2CH_2CO_2H$ ,  $b_7$   $141-2^\circ$ ,<sup>307</sup>  $b_{23}$   $168-70^\circ$ ; n 25/D 1.4778; <sup>305</sup> chloride,  $b_9$   $106-8^\circ$ ; <sup>305</sup>, <sup>307</sup> n 25/D 1.4835.<sup>305</sup>  
 $BuSCH_2CH_2CH_2CO_2H$ ,  $b_{15}$   $163-5^\circ$ .<sup>50</sup>  
 $C_8H_{17}SCH_2CH_2CH_2CO_2H$ , m.  $36^\circ$ ; <sup>169</sup>, <sup>345</sup>  $b_{0.5}$   $155-8^\circ$ .<sup>345</sup>  
 $MeSCH_2CH_2CH_2CH_2CO_2H$ ,  $b_9$   $129-30^\circ$ .<sup>305</sup>  
 $C_7H_{15}SCH_2CH_2CH_2CH_2CO_2H$ , m.  $28^\circ$ ;  $b_1$   $163.5-5^\circ$ .<sup>169</sup>, <sup>345</sup>  
 $C_6H_{13}S(CH_2)_5CO_2H$ , m.  $28^\circ$ ;  $b_1$   $164-6^\circ$ .<sup>169</sup>, <sup>345</sup>  
 $PrS(CH_2)_8CO_2H$ , m.  $28^\circ$ ; <sup>345</sup>  $b_2$   $165-70^\circ$ .<sup>169</sup>, <sup>345</sup>  
 $MeS(CH_2)_{10}CO_2H$ , m.  $45^\circ$ ;  $b_1$   $165-8^\circ$ .<sup>169</sup>, <sup>345</sup>

### Arylmercapto Monocarboxylic Acids

- $PhSCHMeCO_2H$ , m.  $20.7^\circ$ ;  $b_9$   $168-70^\circ$ ; D-[ $\alpha$ ] 25/D 123.9°, L-[ $\alpha$ ] 25/D  $-123^\circ$ ; D-amide, m.  $146.5^\circ$ ; <sup>343</sup> Et ester,  $b_{15}$   $139.5^\circ$ .<sup>340b</sup>  
 $PhCH_2SCHMeCO_2H$ , m.  $83^\circ$ ,<sup>192</sup>  $79^\circ$ ,<sup>324</sup>  $76.5^\circ$ ,<sup>304</sup>  $74^\circ$ ; <sup>225</sup> n 18/D 1.5503.<sup>324</sup>

- $\beta$ -C<sub>10</sub>H<sub>7</sub>SCHMeCO<sub>2</sub>H, D m. 54°; L m. 53.5°. <sup>295</sup>  
 PhCH<sub>2</sub>SCHEtCO<sub>2</sub>H, b<sub>1</sub> 150–2°; amide, m. 107°; <sup>62</sup> *p*-toluide, m. 75°. <sup>286</sup>  
 PhSCHPhCO<sub>2</sub>H, m. 103°. <sup>153</sup>  
 PhSCHMe<sub>2</sub>CO<sub>2</sub>H, m. 66°. <sup>277</sup>  
 PhCH<sub>2</sub>SCMe<sub>2</sub>CO<sub>2</sub>H, m. 131°, <sup>277</sup> 97°. <sup>225</sup>  
 PhCH<sub>2</sub>CH<sub>2</sub>SCMe<sub>2</sub>CO<sub>2</sub>H, m. 69°. <sup>277</sup>  
 Ph<sub>3</sub>CSCMe<sub>2</sub>CO<sub>2</sub>H, m. 156°. <sup>225</sup>  
 PhSCMePhCO<sub>2</sub>H, m. 105°; Et ester, b<sub>10</sub> 183°; d 20/4 1.125; n 20/D 1.5785; amide, m. 89°. <sup>49</sup>  
 PhSCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 61°, <sup>172a</sup>, <sup>212b</sup> 58°; <sup>169</sup> Me ester, b<sub>12</sub> 153.5°; d 20/4 1.140; n 20/D 1.5510. <sup>215</sup>  
 PhCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 84°, <sup>208b</sup> 83°, <sup>324</sup> 81.5°, <sup>215</sup> 80.5°; <sup>169</sup> Me ester, b<sub>14</sub> 173°; d 20/4 1.117; n 20/D 1.5414; <sup>215</sup> Et ester, b<sub>1.7</sub> 134–6°, <sup>413</sup> b<sub>0.22</sub> 101–3°; n 25/D 1.5305, <sup>397</sup> n 20/D 1.5329. <sup>413</sup>  
 PhCHMeSCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 59°. <sup>209b</sup>  
 PhCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 47°. <sup>209b</sup>  
 Ph<sub>2</sub>CHSCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 90°. <sup>225</sup>  
*p*-MeC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, b<sub>6</sub> 153–5°. <sup>292</sup>  
*o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 147°; anilide, m. 166°. <sup>130</sup>  
*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 131°. <sup>35</sup>  
*p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 129°; Ac., m. 203°. <sup>35</sup>  
*p*-BrC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 115°. <sup>74</sup>  
*p*-HSC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 85°. <sup>35</sup>  
*p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CPh<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 126°. <sup>225</sup>  
 3,5-I<sub>2</sub>C<sub>3</sub>H<sub>2</sub>N·SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H-4, m. 213°. <sup>252</sup>  
 PhSCHMeCH<sub>2</sub>CO<sub>2</sub>H, n 18/D 1.5503; <sup>324</sup> amide, m. 93.5°. <sup>359</sup>  
 PhCH<sub>2</sub>SCHMeCH<sub>2</sub>CO<sub>2</sub>H, b<sub>1</sub> 159–60°; amide, m. 85°. <sup>62</sup>  
 PhSCH<sub>2</sub>CHMeCO<sub>2</sub>H, m. 45°; <sup>271a</sup> Me ester, b<sub>13</sub> 154°; d 20/4 1.109; n 20/D 1.5406. <sup>215</sup>  
 PhCH<sub>2</sub>SCH<sub>2</sub>CHMeCO<sub>2</sub>H, m. 43°; <sup>271a</sup> Me ester, b<sub>13</sub> 169.5°; d 20/4 1.089; n 20/D 1.5323. <sup>215</sup>  
 PhCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CHMeCO<sub>2</sub>H, b<sub>6</sub> 190–5°; d 20/4 1.1207; n 20/D 1.5450. <sup>271a</sup>  
 PhCH<sub>2</sub>SCHEtCH<sub>2</sub>CO<sub>2</sub>H, b<sub>1</sub> 150–2°; amide, m. 107°. <sup>62</sup>  
 PhSCH(CHMe<sub>2</sub>)CH<sub>2</sub>CONH<sub>2</sub>, m. 80.5°. <sup>359</sup>  
 PhSCH(CMe<sub>3</sub>)CH<sub>2</sub>CONH<sub>2</sub>, m. 98°. <sup>359</sup>  
 PhSCHPhCH<sub>2</sub>CO<sub>2</sub>H, m. 105°; D m. 88, L m. 88; Et ester, b<sub>10</sub> 183°; d 20/4 1.125; n 26/D 1.5785; amide, m. 89°; D m. 104°, L m. –104°. <sup>49</sup>

$\text{PhCH}_2\text{SCHPhCH}_2\text{CO}_2\text{H}$ , m.  $81^\circ$ .<sup>62</sup>  
 $p\text{-MeC}_6\text{H}_4\text{SCHPhCH}_2\text{CO}_2\text{H}$ , m.  $60^\circ$ .<sup>318b</sup>  
 $\text{PhSCMe}_2\text{CH}_2\text{CO}_2\text{H}$ ,  $b_{12}$   $196^\circ$ .<sup>408</sup>  
 $\text{PhSCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $69^\circ$ ,<sup>15</sup>  $63^\circ$ ,<sup>75</sup>  $60^\circ$ ; <sup>33</sup>  $b_5$   $182^\circ$ ,<sup>15</sup>  $b_{19}$   $212^\circ$ ; chloride,  $b_{10}$   $168\text{--}70^\circ$ ; amide, m.  $91^\circ$ .<sup>75</sup>  
 $p\text{-MeC}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $81^\circ$ ;  $b_4$   $180^\circ$ .<sup>15</sup>  
 $\beta\text{-C}_{10}\text{H}_7\text{SCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $89^\circ$ .<sup>15</sup>  
 $\text{PhSCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $57^\circ$ ;  $b_{20}$   $222^\circ$ ; <sup>75</sup> Et ester,  $b_{0.2}$   $121\text{--}4^\circ$ ; <sup>33</sup> chloride,  $b_{20}$   $177^\circ$ ; amide, m.  $99^\circ$ .<sup>75</sup>

### Alkyl- and Arylmercapto Unsaturated Acids

$\text{EtSCH:CHCO}_2\text{H}$ , m.  $84^\circ$ .<sup>140b</sup>  
 $\text{BuSCH:CHCO}_2\text{Et}$ ,  $b_2$   $100\text{--}7^\circ$ ; d 20/4 0.9992; n 20/D 1.4990.<sup>99</sup>  
 $\text{OctSCH:CHCO}_2\text{Et}$ ,  $b_{0.23\text{--}0.3}$   $130\text{--}4^\circ$ ; n 20/D 1.4941–50.<sup>99</sup>  
 $t\text{-C}_{12}\text{H}_{25}\text{SCH:CHCO}_2\text{Et}$ ,  $b_{0.42\text{--}0.6}$   $138\text{--}52^\circ$ ; n 20/D 1.5005.<sup>99</sup>  
 $\text{PhSCH:CHCO}_2\text{H}$ , m.  $128.5^\circ$ ,<sup>98</sup>  $122^\circ$ ; Et ester,  $b_{2-3}$   $145\text{--}50^\circ$ .<sup>97</sup>  
 $\text{PhCH}_2\text{SCH:CHCO}_2\text{H}$ , *cis*, m.  $145^\circ$ ; *trans*, m.  $163^\circ$ ; *cis* and *trans*, m.  $126^\circ$ .<sup>324</sup>  
 $p\text{-MeC}_6\text{H}_4\text{SCH:CHCO}_2\text{H}$ , m.  $107^\circ$ .<sup>98</sup>  
 $p\text{-ClC}_6\text{H}_4\text{SCH:CHCO}_2\text{H}$ , m.  $98\text{--}112^\circ$ .<sup>98</sup>  
 $3,4\text{-Cl}_2\text{C}_6\text{H}_3\text{SCH:CHCO}_2\text{H}$ , m.  $98\text{--}128^\circ$ .<sup>98</sup>  
 $\text{MeSCMe:CHCO}_2\text{Me}$ , m.  $58^\circ$ ;  $b_{12}$   $117^\circ$ .<sup>369</sup>  
 $\text{EtSCMe:CHCO}_2\text{H}$ , *normal*, m.  $113^\circ$ ; <sup>9</sup> Me ester,  $b_{14}$   $116\text{--}32^\circ$ ; Et ester, b.  $238^\circ$ ,<sup>370</sup>  $b_{766}$   $195^\circ$ ,<sup>335a</sup>  $b_{15}$   $114\text{--}7^\circ$ ,<sup>347</sup>  $b_{16}$   $139\text{--}41^\circ$ ; <sup>370</sup> *iso*, m.  $92^\circ$ ,<sup>9</sup>  $91^\circ$ ,<sup>335a</sup>  $86^\circ$ ; <sup>347</sup> Et ester, b.  $232\text{--}6^\circ$ ,  $b_{14}$   $125\text{--}6^\circ$ ,  $b_{16}$   $127\text{--}9^\circ$ .<sup>370</sup>  
 $\text{PrSCMe:CHCO}_2\text{H}$ , m.  $70^\circ$ ; Et ester,  $b_{15}$   $117\text{--}20^\circ$ .<sup>347</sup>  
 $\text{AmSCMe:CHCO}_2\text{Et}$ ,  $b_{15}$   $126\text{--}8^\circ$ .<sup>347</sup>  
 $\text{PhSCMe:CHCO}_2\text{H}$ , m.  $177^\circ$ .<sup>128</sup>  
 $\text{PhCH}_2\text{SCMe:CHCO}_2\text{H}$ , m.  $134^\circ$ ,<sup>347</sup> 2 isomers, m.  $130^\circ$  and  $194^\circ$ ; <sup>9</sup> Me ester, m.  $73^\circ$ ,<sup>369</sup>  $70^\circ$ ; Et ester, m.  $64.5^\circ$ ,<sup>370</sup>  $68^\circ$ ;  $b_{15}$   $155\text{--}60^\circ$ ; <sup>347</sup> *iso* Et ester,  $b_{12}$   $193^\circ$ .<sup>369</sup>  
 $\text{PhSCPh:CHCO}_2\text{H}$ , m.  $193^\circ$ .<sup>76</sup>  
 $\text{PhCH}_2\text{SC}(:\text{CHOMe})\text{CH}_2\text{CO}_2\text{H}$ , m.  $67^\circ$ .<sup>324</sup>

### Substituted Sulfide-Acids

#### Hydroxy and Ether Acids

$\text{HOCH}_2\text{SCH}_2\text{CO}_2\text{H}$ , anilide, m.  $92^\circ$ .<sup>380a</sup>  
 $\text{HOCHPrSCH}_2\text{CO}_2\text{H}$ , anilide, m.  $75^\circ$ .<sup>380a</sup>

- HOCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, lactone, m. 45–50°; *p*-aniside, m. 78°;  
*p*-phenetide, m. 81°. <sup>28d</sup>
- HOCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Me, b<sub>18</sub> 159–63°, <sup>351</sup> b<sub>9</sub> 138.5°, b<sub>19</sub> 153°;  
 d 20/4 1.161; n 20/D 1.4908. <sup>215</sup>
- HOCH<sub>2</sub>CH<sub>2</sub>S(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H, m. 69°. <sup>351</sup>
- PhCH<sub>2</sub>SCH(OH)CO<sub>2</sub>H, m. 128°. <sup>415</sup>
- PhSCMe(OH)CO<sub>2</sub>H, m. 87°, <sup>128</sup> 85°. <sup>391d</sup>
- PhCH<sub>2</sub>SCMe(OH)CO<sub>2</sub>H, m. 82°. <sup>335b</sup>
- 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SCH<sub>2</sub>CH(OH)CO<sub>2</sub>H, m. 168°. <sup>257</sup>
- MeSCH<sub>2</sub>CH<sub>2</sub>CH(OH)CO<sub>2</sub>H, S-benzyl isothiuronium salt, m.  
 157°. <sup>203</sup>
- PhCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CHOH(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>H, m. 63°. <sup>393</sup>
- PhOCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 48°. <sup>394</sup>
- PhOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>1</sub> 185°; Me ester, b<sub>2-3</sub> 170–8°. <sup>394</sup>
- BuOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>1</sub> 160°; n 25/D 1.4790. <sup>394</sup>
- PhCH<sub>2</sub>SCH(CH<sub>2</sub>CH<sub>2</sub>OMe)CO<sub>2</sub>H, m. 67°. <sup>324</sup>
- PhCH<sub>2</sub>SCH(CH<sub>2</sub>OMe)CH<sub>2</sub>CO<sub>2</sub>H, n 18/D 1.5453. <sup>324</sup>

### Halogen Substituted

- ClCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Me, b<sub>9</sub> 125°; d 25/4 1.1953; n 25/D  
 1.4920. <sup>351</sup>
- MeSCCl<sub>2</sub>CO<sub>2</sub>Me, b<sub>12</sub> 92°. <sup>44</sup>
- EtSCH<sub>2</sub>CHClCO<sub>2</sub>Me, b<sub>12</sub> 96–100°. <sup>56</sup>
- Me<sub>2</sub>CHSCH<sub>2</sub>CHClCO<sub>2</sub>Me, b<sub>12</sub> 101°. <sup>56</sup>
- CCl<sub>3</sub>CH(OH)SCH<sub>2</sub>CO<sub>2</sub>H, anilide, m. 112°. <sup>380a</sup>
- PhCHBrCHBrSCH<sub>2</sub>CO<sub>2</sub>H, m. 109–12°. <sup>210</sup>

### Keto Substituted

- MeCOCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 45°; b<sub>11</sub> 183–5°; <sup>378b</sup> amide, m. 144°. <sup>392</sup>
- PhCOCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 102°, <sup>206a</sup> 101°; <sup>31</sup>, <sup>392</sup> amide, m. 158°; <sup>392</sup>  
 oxime, m. 127°. <sup>206a</sup>
- PhCOCHPhSCH<sub>2</sub>CO<sub>2</sub>H, m. 105°. <sup>31</sup>
- PhCOCH<sub>2</sub>CHPhSCH<sub>2</sub>CO<sub>2</sub>H, m. 129°. <sup>318a</sup>
- p*-AcHNCC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 92.5°. <sup>134</sup>
- PhCOCHPhSCHMeCO<sub>2</sub>H, m. 111° and 155°. <sup>225</sup>
- PhCOCHPhSCMe<sub>2</sub>CO<sub>2</sub>H, m. 130°. <sup>225</sup>
- PhCOCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 46–9°; hydrate, m. 62°. <sup>208c</sup>
- OC(CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 150°. <sup>378a</sup>
- MeSCH(COMe)CO<sub>2</sub>Et, b<sub>14</sub> 140°. <sup>56</sup>
- MeSCH(CH<sub>2</sub>COPh)CO<sub>2</sub>H, m. 63°. <sup>51</sup>

- PhSCH(CH<sub>2</sub>COPh)CO<sub>2</sub>H, m. 123°. <sup>51</sup>  
 PhCH<sub>2</sub>SCH(CH<sub>2</sub>COPh)CO<sub>2</sub>H, m. 134°. <sup>51</sup>  
 MeSCH<sub>2</sub>COCO<sub>2</sub>H, m. 147°, <sup>330</sup> 149°; <sup>329</sup> Et ester, b<sub>15</sub> 105°. <sup>329</sup>, <sup>330</sup>  
 PhCH<sub>2</sub>SCH<sub>2</sub>COCO<sub>2</sub>H, m. 128°. <sup>329</sup>  
*p*-MeC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>COCO<sub>2</sub>H, m. 123°. <sup>329</sup>  
*p*-ClC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>COCO<sub>2</sub>H, m. 137°. <sup>329</sup>  
*p*-BrC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>COCO<sub>2</sub>H, m. 143°. <sup>329</sup>  
*p*-IC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>COCO<sub>2</sub>H, m. 152°. <sup>329</sup>  
 PhCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CO(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>H, m. 65°. <sup>393</sup>  
 3-(2-Me-1,4-naphthoquinone)SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 161°. <sup>178</sup>

*Pyridyl- and Quinolylmercaptoacids*

- 2-pyridylSCH<sub>2</sub>CO<sub>2</sub>H, anhydro compound, m. 180°. <sup>119</sup>  
 3,5-I<sub>2</sub>C<sub>5</sub>H<sub>2</sub>N·SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H-4, m. 213°. <sup>252</sup>  
 2-quinolylSCH<sub>2</sub>CO<sub>2</sub>H, m. 90°; anhydro compound, m. 194°;  
 Et ester, m. 91.5°; amide, m. 126°. <sup>119</sup>  
 4-Me-2-quinolylSCH<sub>2</sub>CO<sub>2</sub>H, m. 117°; anhydro compound, m.  
 227°. <sup>119</sup>  
 3,4-Me<sub>2</sub>-2-quinolylSCH<sub>2</sub>CO<sub>2</sub>H, m. 134°; anhydro compound, m.  
 225°. <sup>119</sup>  
 4,8-Me<sub>2</sub>-2-quinolylSCH<sub>2</sub>CO<sub>2</sub>H, m. 132°. <sup>119</sup>  
 2-quinolylSCHMeCO<sub>2</sub>H, m. 101°; anhydro compound, m. 148°. <sup>119</sup>  
 4-Me-2-quinolylSCHMeCO<sub>2</sub>H, m. 139°; anhydro compound, m.  
 136°. <sup>119</sup>  
 2-quinolylSCHEtCO<sub>2</sub>H, m. 114°; anhydro compound, m. 162°. <sup>119</sup>  
 2-quinolylSCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 87°. <sup>119</sup>

*Miscellaneous*

- NCCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, m. 73°; <sup>394</sup> Me ester, b<sub>3</sub> 103°; <sup>421</sup> Et  
 ester, b<sub>3</sub> 120–5°, <sup>308</sup> b<sub>16</sub> 169°; d 20/4 1.126; n 20/D 1.4810. <sup>215</sup>  
 NCCH<sub>2</sub>CH:CHCH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>Et, b<sub>0.3</sub> 136–40°. <sup>131</sup>  
 HSCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 37.5°; b<sub>2</sub> 166–71°; Et ester, b<sub>9</sub>  
 149–50°. <sup>351</sup>  
 HSCH<sub>2</sub>CH<sub>2</sub>S(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H, m. 119°. <sup>351</sup>  
 NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et, b<sub>0.5–0.6</sub> 115–118°. <sup>39</sup>  
 Me<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>7</sub> 143–4°; n 20/D 1.4811. <sup>57</sup>  
 Et<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>12</sub> 184–6°. <sup>272d</sup>  
 Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>9</sub> 164–6°; n 20/D 1.4790. <sup>57</sup>  
 Me<sub>3</sub>SiOSiMe<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>H, b<sub>2</sub> 149–50.2°; d<sub>20</sub> 0.9903; n  
 20/D 1.4588. <sup>57</sup>



(EtO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SCH<sub>2</sub>CO<sub>2</sub>Et, b<sub>50</sub> 200–1.5°; d 20/4 1.0301; n 20/D 1.4479.<sup>68</sup>

### Sulfide Benzoic Acids

- o*-MeSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, dipole moment 2.47.<sup>136</sup>  
*m*-MeSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 129°;<sup>116, 446</sup> 127°;<sup>336, 388</sup> 126°;<sup>20, 52, 405</sup> Et ester, b<sub>8</sub> 148–8.2°;<sup>336</sup> chloride, b<sub>8</sub> 123°;<sup>116</sup> —CONHCH<sub>2</sub>CH<sub>2</sub>NEt<sub>2</sub>, citrate, m. 74°.<sup>291</sup>  
*p*-MeSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 192°;<sup>20, 336</sup> 190°;<sup>387</sup> Et ester, m. 28°; b<sub>15</sub> 168°;<sup>245</sup> b<sub>14</sub> 170–4.5°;<sup>20</sup> n 20/D 1.5784;<sup>336</sup> chloride, m. 54°;<sup>78, 79</sup> amide, m. 191°;<sup>72</sup> —CONHNHSO<sub>2</sub>Ph, m. 237°.<sup>20</sup>  
*o*-EtSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 134°; chloride, b<sub>3</sub> 133°.<sup>116</sup>  
*m*-EtSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 98°; chloride, b<sub>3</sub> 127°.<sup>116</sup>  
*p*-EtSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 146°;<sup>10</sup> 145°; chloride, b<sub>3</sub> 118°;<sup>116</sup> amide, m. 170°; anilide, m. 158°.<sup>10</sup>  
*o*-PrSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 124°;<sup>418</sup> 121°; chloride, b<sub>3</sub> 145°.<sup>116</sup>  
*m*-PrSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 104°; chloride, b<sub>3</sub> 138°.<sup>116</sup>  
*p*-PrSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 145°.<sup>72</sup>  
*o*-BuSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 98°; chloride, b<sub>3</sub> 151°.<sup>116</sup>  
*m*-BuSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 103°; chloride, b<sub>3</sub> 147°;<sup>116</sup> b. 185–7°; Me ester, b<sub>16</sub> 172°; amide, m. 96°; —CONHCH<sub>2</sub>CH<sub>2</sub>NEt<sub>2</sub>, citrate, m. 74°.<sup>291</sup>  
*p*-BuSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 122°.<sup>72</sup>  
*o*-CH<sub>2</sub>:CHCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 114°.<sup>418</sup>  
*o*-CH<sub>3</sub>CH:CHSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 146°.<sup>418</sup>  
2-C<sub>4</sub>H<sub>3</sub>S-SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*, m. 197°; amide, m. 201°.<sup>403</sup>  
3-C<sub>4</sub>H<sub>3</sub>S-SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*, m. 191°.<sup>402</sup>  
3-(2,5-Me<sub>2</sub>C<sub>4</sub>HS)SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*, m. 199.5°.<sup>401</sup>  
*o*-PhSC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 166°.<sup>435</sup>  
*p*-PhCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 190°; Et ester, m. 60°.<sup>126</sup>  
*o*-HOCH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 126°.<sup>157</sup>  
5,2-EtS(HO)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, m. 92–5°.<sup>265</sup>  
2,3,5-PrSCL<sub>2</sub>C<sub>6</sub>H<sub>2</sub>CO<sub>2</sub>H, m. 66.5°.<sup>418</sup>  
2,3,5-CH<sub>2</sub>:CHCH<sub>2</sub>SCL<sub>2</sub>C<sub>6</sub>H<sub>2</sub>CO<sub>2</sub>H, m. 87°.<sup>418</sup>  
2,3,5-CH<sub>3</sub>CH:CHSCL<sub>2</sub>C<sub>6</sub>H<sub>2</sub>CO<sub>2</sub>H, m. 74.5°.<sup>418</sup>  
2,5-EtSBrC<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, m. 142°.<sup>265</sup>  
2,4-O<sub>2</sub>N(Cl)C<sub>6</sub>H<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*, m. 156.5°.<sup>296</sup>  
2,5-O<sub>2</sub>N(Cl)C<sub>6</sub>H<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*, m. 189°.<sup>296</sup>  
4,3-MeS(NO<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, m. 240°; Me ester, m. 117°; amide, m. 209°.<sup>115</sup>

- 2,4-EtS(NO<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, m. 212°. <sup>383</sup>  
 4,3-EtS(NO<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, m. 231°; Me ester, m. 130°; amide, m. 214°. <sup>115</sup>  
 4,3-PrS(NO<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, m. 234°; Me ester, m. 97°; amide, m. 187°. <sup>115</sup>  
 4,3-PhCH<sub>2</sub>S(NO<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, m. 216°; Me ester, m. 138°. <sup>115</sup>  
 2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*, m. 180°; Me ester, m. 117.5°. <sup>296</sup>  
 2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*, m. 241°; Me ester, m. 181.5°. <sup>296</sup>  
 4,3-MeS(NH<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, Me ester, m. 61°; b<sub>4</sub> 170°; amide, m. 166°. <sup>115</sup>  
 2,4-EtS(NH<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, m. 146°. <sup>383</sup>  
 4,3-EtS(NH<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, Me ester, b<sub>4</sub> 180°; n 23/D 1.5936; amide, m. 156°. <sup>115</sup>  
 5,2-EtS(NH<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>Et, m. 138°. <sup>265</sup>  
 4,3-PrS(NH<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, Me ester, m. 24°; b<sub>6</sub> 182°; n 24.5/D 1.5936; amide, m. 118°. <sup>115</sup>  
 4,3-PhCH<sub>2</sub>S(NH<sub>2</sub>)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>Me, m. 76–8°; b<sub>4.5</sub> 234°. <sup>115</sup>  
*o*-PhSOCH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 202°. <sup>143</sup>  
*o*-PhSO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 203°. <sup>144</sup>  
*o*-MeSC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 128°; amide, m. 165°. <sup>258</sup>  
*p*-MeSC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 94°; Me ester, b<sub>3</sub> 179–81°; —CONH-CH<sub>2</sub>CH<sub>2</sub>OH, m. 117°. <sup>95</sup>  
*p*-PhSC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CO<sub>2</sub>H, b<sub>0.05</sub> 163°; —CONHCH<sub>2</sub>CH<sub>2</sub>OH, m. 90°. <sup>95</sup>  
*p*-MeSC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H, m. 54°, <sup>71</sup> 49°. <sup>73</sup>  
*p*-MeSC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>4</sub>CO<sub>2</sub>H, m. 82°; amide, m. 128°. <sup>73</sup>  
*p*-MeSC<sub>6</sub>H<sub>4</sub>CO(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H, m. 157°, <sup>71</sup> 153°. <sup>73</sup>  
*p*-MeSC<sub>6</sub>H<sub>4</sub>CO(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>H, m. 136°; Et ester, m. 44°. <sup>73</sup>  
 RSCHPhNHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*, R *i*-Pr, m. 99°; Bu, m. 92°; *i*-Bu, m. 96°; *t*-Bu, m. 100°; Ph, m. 98°; *p*-MeC<sub>6</sub>H<sub>4</sub>-, m. 120°. <sup>396</sup>

### Alkyl- and Arylmercapto Dibasic Acids

- MeSCH(CO<sub>2</sub>Et)<sub>2</sub>, b<sub>14</sub> 155°. <sup>56</sup>  
 EtSCH(CO<sub>2</sub>Et)<sub>2</sub>, b<sub>13</sub> 166°. <sup>56</sup>  
 EtS(Et)C(CONH)<sub>2</sub>CO, m. 129°. <sup>175</sup>  
 EtS(PhCH<sub>2</sub>)C(CONH)<sub>2</sub>CO, m. 180°. <sup>175</sup>  
 PhS(Et)C(CONH)<sub>2</sub>CO, m. 184°. <sup>175</sup>  
 PhS(PhCH<sub>2</sub>)C(CONH)<sub>2</sub>CO, m. 227°. <sup>175</sup>  
 MeSCH<sub>2</sub>CMe(CO<sub>2</sub>H)<sub>2</sub>, diMe ester, b<sub>16</sub> 128–33°; diEt ester, b<sub>18</sub> 132–6°; barbiturate, m. 162°. <sup>45</sup>

- $\text{MeSCH}_2\text{CEt}(\text{CO}_2\text{H})_2$ , diEt ester,  $b_{15}$  143–8°; barbiturate, m. 187°. <sup>45</sup>  
 $\text{MeSCH}_2\text{C}(\text{CH}_2\text{Ph})(\text{CO}_2\text{H})_2$ , m. 164°; diEt ester, m. 54°;  $b_{15}$  199°; barbiturate, m. 210°. <sup>45</sup>  
 $\text{EtSCH}_2\text{CMe}(\text{CO}_2\text{H})_2$ , diEt ester,  $b_{13}$  142–6°; barbiturate, m. 151°. <sup>45</sup>  
 $\text{EtSCH}_2\text{CEt}(\text{CO}_2\text{H})_2$ , m. 108°; diEt ester,  $b_{12}$  148–51°; barbiturate, m. 164°. <sup>45</sup>  
 $\text{EtSCH}_2\text{C}(\text{CHMe}_2)(\text{CO}_2\text{H})_2$ , diEt ester,  $b_{12}$  152–6°; barbiturate, m. 136°. <sup>45</sup>  
 $\text{EtSCH}_2\text{CPh}(\text{CO}_2\text{H})_2$ , diEt ester,  $b_{11}$  191–3°; barbiturate, m. 206°. <sup>45</sup>  
 $\text{EtSCH}_2\text{C}(\text{CH}_2\text{Ph})(\text{CO}_2\text{H})_2$ , diEt ester,  $b_{13}$  203–6°; barbiturate, m. 207°. <sup>45</sup>  
 $\text{EtSCHMeCMe}(\text{CO}_2\text{H})_2$ , diMe ester,  $b_{12}$  138–43°; barbiturate, m. 198°. <sup>45</sup>  
 $\text{EtSCHMeCEt}(\text{CO}_2\text{H})_2$ , diEt ester,  $b_{12}$  147–50°; barbiturate, m. 161°. <sup>45</sup>  
 $\text{PhCH}_2\text{SCH}_2\text{CEt}(\text{CO}_2\text{H})_2$ , diEt ester, m. 49°;  $b_{11}$  199–203°; barbiturate, m. 146°. <sup>45</sup>  
 $\text{MeSCH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{H})_2$ ,  $b_{30}$  166–7°;  $b_{745}$  275–80°;  $d$  20/4 1.081;  $n$  25/D 1.4675. <sup>440</sup>  
 $\text{PhCH}_2\text{SCH}_2\text{CHMeCH}(\text{CO}_2\text{Et})_2$ ,  $b_{0.003}$  147°. <sup>256</sup>  
 $\text{PhCH}_2\text{SCH}_2\text{CHMeCMe}(\text{CO}_2\text{H})_2$ , m. 120°; diEt ester,  $b_{0.003}$  136°. <sup>256</sup>  
 $\text{PhSCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{H})_2$ , m. 101°; diEt ester,  $b_{20}$  230°. <sup>75</sup>  
 $\text{MeSCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 133°. <sup>87</sup>  
 $\text{EtSCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 126°, <sup>140a</sup> 119.5°; <sup>87</sup>  $D$  m. 128°;  $[\alpha]$  20/D 139.3°;  $L$  m. 128°;  $[\alpha]$  19/D –139.3°. <sup>140a</sup>  
 $\text{PrSCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 112°. <sup>87</sup>  
 $\text{BuSCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 144.5°. <sup>87</sup>  
 $t\text{-BuSCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 164°. <sup>87</sup>  
 $\text{AmSCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 99.5°. <sup>87</sup>  
 $i\text{-AmSCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 215°. <sup>87</sup>  
 $\text{HexSCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 81°. <sup>87</sup>  
 $\text{C}_9\text{H}_{19}\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 105°; diEt ester,  $b_1$  160–4°. <sup>25</sup>  
 $\text{C}_{11}\text{H}_{23}\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 105°; anhydride, m. 36°; diEt ester,  $b_1$  174–6°. <sup>25</sup>  
 $\text{C}_{12}\text{H}_{25}\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m. 103°, <sup>25</sup> 97.5°; <sup>87</sup> anhydride, m. 46°; diEt ester,  $b_1$  178–84°. <sup>25</sup>

- $C_{14}H_{29}SCH(CO_2H)CH_2CO_2H$ , m.  $104^\circ$ ; anhydride, m.  $52^\circ$ ; diEt ester,  $b_1$   $205^\circ$ .<sup>25</sup>  
 $C_{16}H_{33}SCH(CO_2H)CH_2CO_2H$ , m.  $105^\circ$ ; anhydride, m.  $64^\circ$ ; diEt ester,  $b_1$   $220-4^\circ$ .<sup>25</sup>  
 $C_{18}H_{37}SCH(CO_2H)CH_2CO_2H$ , m.  $105^\circ$ ; anhydride, m.  $68.5^\circ$ ; diEt ester,  $b_2$   $238-42^\circ$ .<sup>25</sup>  
 $C_8H_{11}SCH(CO_2H)CH_2CO_2H$ , m.  $151^\circ$ .<sup>437a</sup>  
 $3-C_4H_9S-SCH(CO_2H)CH_2CO_2H$ , m.  $131^\circ$ .<sup>59</sup>  
 $PhCH_2SCH(CO_2H)CH_2CO_2H$ , m.  $186^\circ$ .<sup>157</sup>  
 $PhCH_2SCH_2CH(CO_2H)CH_2CO_2H$ , m.  $109^\circ$ ; anhydride, m.  $58.5^\circ$ ; diMe ester,  $b_{0.7}$   $154-6^\circ$ ;  $n$  25/D 1.5250.<sup>397</sup>

- $EtSCH:C(CO_2Et)_2$ ,  $b_{0.2}$   $127^\circ$ .<sup>176</sup>  
 $MeSC(CH_2CO_2Et):CHCO_2Et$ ,  $b_6$   $135^\circ$ .<sup>303b</sup>  
 $EtSC(CH_2CO_2H):CHCO_2H$ , m.  $155-63^\circ$ .<sup>335a</sup>  
 $EtSC(CH_2CO_2H):CBrCO_2H$ , m.  $131-41^\circ$ .<sup>140b</sup>

### Symmetrical Dibasic Acids

- $S(CO_2Et)_2$ , b.  $180^\circ$ .<sup>299</sup>  
 $S(CH_2CO_2H)_2$ , m.  $129^\circ$ ,<sup>7, 114, 205a, 377, 379, 381a</sup>  $126^\circ$ ; <sup>441</sup>  $K_1$   $4.9 \times 10^{-2}$ , <sup>287c</sup>  $4.8 \times 10^{-2}$ ; <sup>233</sup>  $K_2$   $3.5 \times 10^{-5}$ ; <sup>273a</sup> conductivity; <sup>2, 284, 323, 439</sup> anhydride, m.  $102^\circ$ ,<sup>7</sup>  $101^\circ$ ;  $b_{12}$   $158-9^\circ$ ,<sup>269</sup>  $b_{10}$   $158^\circ$ ; <sup>7</sup> acid salts HK, m.  $129^\circ$ ;  $H_3K$ , m.  $229^\circ$ ; <sup>118</sup> diMe ester,  $b_{11}$   $135^\circ$ ; <sup>7</sup> diEt ester, b.  $267-8^\circ$ ,<sup>441</sup>  $240-50^\circ$ ; <sup>381b</sup> diBu ester,  $b_2$   $131^\circ$ ; <sup>266</sup> imide, m.  $128^\circ$ ,<sup>22, 381b</sup> Bz, m.  $153^\circ$ ; Phenyl imide, m.  $212^\circ$ ; <sup>346</sup> thioamide, m.  $125^\circ$ ; <sup>448</sup> monoanilide, m.  $103^\circ$ ; <sup>28b</sup> dianilide, m.  $168^\circ$ ,<sup>7</sup>  $167^\circ$ ,<sup>28a</sup>  $158^\circ$ ,<sup>423</sup>  $147^\circ$ ,<sup>313</sup> Bz, m.  $146^\circ$ ; <sup>423</sup> mono-*p*-toluide, m.  $102^\circ$ ,<sup>28c</sup>  $95^\circ$ ; <sup>7</sup> Me ester-*p*-toluide, m.  $39^\circ$ ; Et ester-*p*-toluide, m.  $47^\circ$ ; <sup>28c</sup> di-*p*-phenetide, m.  $114^\circ$ .<sup>28c</sup>  
 $S(CHMeCO_2H)_2$ , DL-m.  $126.5^\circ$ ,<sup>146a</sup>  $125^\circ$ ; <sup>147b, 286c, 287a, 287c</sup>  $K_1 + K_2$   $K_2$   $2.4 \times 10^{-5}$ ; <sup>273a</sup> affinity K 0.049; <sup>286c, 287c</sup> D- and L-m.  $117^\circ$ ,  $[\alpha]$   $197^\circ$  and  $-198^\circ$ ; <sup>147b</sup> *meso*, m.  $109^\circ$ ; affinity K 0.044,<sup>286c</sup>  $K_2$   $2.7 \times 10^{-5}$ ; <sup>273a</sup> eutectics; <sup>146a, 146d</sup> anhydride  $b_{14}$   $133-7^\circ$ ;  $n$  20/D 1.5010; <sup>269</sup> imide 2 forms, m.  $129^\circ$  and  $72^\circ$ .<sup>346</sup>  
 $S(ChEtCO_2H)_2$ , *meso*-m.  $109^\circ$ ,<sup>3a</sup>  $109.5^\circ$ ,<sup>3b</sup>  $105^\circ$ ; <sup>287a</sup>  $K_2$   $2.6 \times 10^{-5}$ ; <sup>273a</sup> DL-m.  $82^\circ$ ,<sup>3a</sup>  $84^\circ$ ; <sup>3b</sup> L-m.  $35^\circ$ ,  $[\alpha]$   $-152^\circ$ ; <sup>3a</sup>  $K_2$   $2.5 \times 10^{-5}$ ; <sup>273a</sup> anhydride, m.  $15^\circ$ ;  $b_{15}$   $149-50^\circ$ ;  $n$  20/D 1.4942; <sup>269</sup> imide, m.  $117^\circ$ ; phenyl imide 2 forms, m.  $123^\circ$  and  $62^\circ$ .<sup>346</sup>

- $S(CH(CHMe_2)CO_2H)_2$ , *meso*-m.  $136^\circ$ ; <sup>3a</sup>  $K_2$   $1.4 \times 10^{-5}$ ; <sup>273a</sup> DL-m.  $118^\circ$ , <sup>3a</sup>  $K_2$   $1.6 \times 10^{-5}$ ; <sup>273a</sup> L-m.  $81.5^\circ$ ,  $[\alpha]$  25/D  $-126.5^\circ$ ; D-m.  $81^\circ$ ;  $[\alpha]$  18/D  $129^\circ$ ; diEt ester,  $b_{13}$   $160-2^\circ$ .<sup>3a</sup>  
 $S(CMe_2CO_2H)_2$ , m.  $142^\circ$ ; <sup>276b</sup>  $138^\circ$ ; <sup>195a</sup>  $K_1$   $2.5 \times 10^{-4}$ ,  $K_2$   $2.3 \times 10^{-5}$  at  $18^\circ$ ; <sup>276b</sup> imide, m.  $157^\circ$ ; methyl imide, m.  $120^\circ$ .<sup>346</sup>  
 $S(CH_2CH_2CO_2H)_2$ , m.  $137.5^\circ$ ,<sup>169</sup>  $134^\circ$ ,<sup>293</sup>  $133^\circ$ ,<sup>2</sup>  $130^\circ$ ,<sup>161</sup>, <sup>314</sup>, <sup>375</sup>  $128^\circ$ ,<sup>172a</sup>, <sup>286d</sup>  $126^\circ$ ; <sup>14</sup>  $K_1 + K_2$ ; <sup>2</sup>  $k$   $7.8 \times 10^{-3}$ ; <sup>286c</sup>, <sup>286d</sup>, <sup>287c</sup> diMe ester  $b_{10}$   $158-9^\circ$ ,<sup>293</sup>  $b_8$   $148.5-9^\circ$ ,<sup>161</sup>  $b_{18}$   $162^\circ$ ; <sup>133c</sup> d 20/4 1.154; n 20/D 1.4750; <sup>161</sup> diEt ester,  $b_{15}$   $174^\circ$ ; d 20/4 1.1034; n 20/ $\alpha$  1.4694, n 20/ $\beta$  1.4791; <sup>36</sup> diDod ester, m.  $39^\circ$ ; diCet ester, m.  $53.5^\circ$ ; <sup>293</sup> diamide, m.  $178.5^\circ$ ,<sup>36</sup>  $182^\circ$ ; di-N-Dod-amide, m.  $140^\circ$ ; di-N-Cet-amide, m.  $131^\circ$ ; <sup>293</sup> dianilide, m.  $163.5^\circ$ ,<sup>36</sup>  $165^\circ$ ; di-*p*-toluide, m.  $199^\circ$ .<sup>293</sup>  
 $S(CH_2CH_2CONHCO_2H)_2$ , diEt ester, m.  $187^\circ$ ; di-*i*-Bu ester, m.  $127^\circ$ ; diAm ester, m.  $137.5^\circ$ .<sup>150</sup>  
 $S(CHMeCH_2CO_2H)_2$ , m.  $85^\circ$  and  $64^\circ$ ; <sup>289</sup> diMe ester,  $b_{13}$   $152^\circ$ ,  $b_{15}$   $156^\circ$ ; <sup>8</sup> diEt ester,  $b_{12}$   $80^\circ$ ; <sup>367</sup> diBu ester,  $b_3$   $141^\circ$ ; <sup>82</sup> ( $-CH_2-CHEtBu$  ester)<sub>2</sub>,  $b_1$   $200-1^\circ$ ; n 20/D 1.4656.<sup>180</sup>  
 $S(CH_2CHMeCO_2H)_2$ , m  $115^\circ$ ;  $K_1$   $1.4 \times 10^{-4}$ ,  $K_2$   $7.9 \times 10^{-6}$  at  $18^\circ$ .<sup>276b</sup>  
 $S(CH_2CMe_2CO_2H)_2$ , m.  $163^\circ$ .<sup>78</sup>, <sup>79</sup>  
 $S(CH_2CH_2CH_2CO_2H)_2$ , m.  $100^\circ$ ,<sup>271d</sup>  $99^\circ$ ; <sup>14</sup>, <sup>146b</sup> diMe ester,  $b_{20}$   $170^\circ$ ; n 20/D 1.4791; diEt ester,  $b_{11}$   $185^\circ$ ,  $b_{23}$   $196^\circ$ ; n 20/D 1.4701; <sup>105</sup> diamide, m.  $152^\circ$ .<sup>41</sup>  
 $S(CH_2CH_2CH_2CH_2CO_2H)_2$ , m.  $96^\circ$ ; <sup>221</sup>, <sup>272c</sup> diMe ester,  $b_{12}$   $205-10^\circ$ .<sup>272c</sup>  
 $S(CMe:CHCO_2H)_2$ , m.  $215^\circ$ ; sol. water 0.1 at  $20^\circ$ ; diMe ester, m.  $23.5^\circ$ ;  $b_{0.6}$   $116-7^\circ$ ; diEt ester,  $b_4$   $150-3^\circ$ ,<sup>368</sup>  $b_{15}$   $155^\circ$ ; <sup>303a</sup> diamide, m.  $192^\circ$ .<sup>368</sup>  
 $S(CH:CMeCO_2H)_2$ , m.  $181^\circ$ ; diMe ester,  $b_5$   $149-50^\circ$ .<sup>368</sup>  
 $S(CH_2CH:CHCH_2CO_2H)_2$ , m.  $155^\circ$ .<sup>131</sup>  
 $S[CH(COMe)CO_2Et]_2$ , m.  $101^\circ$ ,<sup>302</sup>  $90^\circ$ ,<sup>111a</sup>, <sup>259</sup>, <sup>377</sup>  $81^\circ$ ,<sup>64</sup>  $78^\circ$ ,<sup>395</sup>  $76^\circ$ .<sup>65</sup>  
 $S[CMe(OH)CO_2H]_2$ , m.  $94^\circ$ .<sup>110</sup>  
 $\alpha,\alpha'$ -thiodibutyrolactone, m.  $89^\circ$ ,  $b_2$   $205^\circ$ .<sup>13</sup>  
 $S[CH(CH_2CH_2CH_2CH_2NH_2)CO_2H]_2$ , m.  $207^\circ$ .<sup>167</sup>  
 $S(CH_2CH_2SCH_2CO_2H)_2$ , m.  $104^\circ$ .<sup>350</sup>

### Symmetrical Dibasic Aromatic Acids

- $S(C_6H_4CO_2H-o)_2$ , m.  $230^\circ$ ; diMe ester, m.  $84^\circ$ ; diEt ester, m.  $58^\circ$ .<sup>296</sup>

$S[C_6H_3(OH)CO_2H-4,3]_2$ , m.  $274^\circ$ ,<sup>4, 253</sup>  $270^\circ$ ; Ac., m.  $164^\circ$ ; Bz., m.  $129^\circ$ ; diMe ester, m.  $148^\circ$ ,<sup>199</sup>  $147^\circ$ ; <sup>253</sup> Ac., m.  $94^\circ$ ; <sup>4, 199</sup> Bz., m.  $117^\circ$ ; diEt ester, m.  $92^\circ$ ; diPh ester, m.  $158^\circ$ ; Ac., m.  $144^\circ$ ; <sup>199</sup>  $(-CH_2CH_2NMe_2 \text{ ester})_2$ , m.  $270^\circ$ ;  $(-CH_2CH_2N(CH_2)_5 \text{ ester})_2$ , m.  $261^\circ$ ; di(methyl amide), m.  $226^\circ$ ; di(dimethyl amide), m.  $103^\circ$ .<sup>253</sup>  
 $S[C_6H_3(OMe)CO_2H-4,3]_2$ , m.  $157^\circ$ .<sup>199</sup>  
 $S[C_6H_2Br(OH)CO_2H-5,4,3]_2$ , m.  $275^\circ$ ; diMe ester, m.  $133^\circ$ .<sup>199</sup>  
 $S[C_6H_2(OAc)(NO_2)CO_2Me-4,5,3]_2$ , m.  $245^\circ$ .<sup>4</sup>  
 $S[C_6H(OH)_2(NO_2)CO_2Me-2,6,5,3]_2$ , m.  $284^\circ$ .<sup>227</sup>  
 $S[C_6H(OH)(OAc)(NO_2)CO_2Me-2,6,5,3]_2$ , m.  $174^\circ$ .<sup>227</sup>  
 $S[C_6H(OH)(OMe)(NO_2)CO_2Me-2,6,5,3]_2$ , m.  $224^\circ$ .<sup>227</sup>  
 $S[C_{10}H_5(OH)CO_2Me-2,3]_2-\alpha$ , m.  $227^\circ$ ; diAc., m.  $244^\circ$ .<sup>227</sup>

### Unsymmetrical Dibasic Acids

$HO_2CCH_2SCHClCO_2H$ , m.  $99^\circ$ .<sup>270b</sup>  
 $HO_2CCH_2SCH(OH)CO_2H$ , m.  $109^\circ$ .<sup>270b</sup>  
 $HO_2CCH_2SCHMeCO_2H$ , m.  $88^\circ$ ; <sup>286e, 394</sup> K 0.048. <sup>286e, 287c</sup>  
 $HO_2CCH_2SCMe(OH)CO_2H$ , m.  $110^\circ$ ; <sup>48a, 380a</sup> monoanilide, m.  $92^\circ$ .<sup>380a</sup>  
 $HO_2CCH_2SCHEtCONHC_6H_4Me-p$ , Et ester, m.  $48^\circ$ ; amide, m.  $140^\circ$ ; anilide, m.  $136^\circ$ .<sup>28e</sup>  
 $HO_2CCH_2SCMe_2CO_2H$ , m.  $111^\circ$ ,<sup>276a</sup>  $107.5^\circ$ ; <sup>149</sup>  $K_1 3.3 \times 10^{-4}$ ,  $K_2 2.0 \times 10^{-6}$  at  $18^\circ$ .<sup>276a</sup>  
 $HO_2CCHMeSCMe_2CO_2H$ , m.  $111^\circ$ ;  $K_1 2.4 \times 10^{-4}$ ,  $K_2 1.5 \times 10^{-5}$  at  $18^\circ$ .<sup>276a</sup>  
 $HO_2CCHMeSCMeEtCO_2H$ , 4 DL-forms, m.  $133^\circ$ ,  $133^\circ$ ,  $93^\circ$ , and  $89^\circ$ .<sup>3b</sup>  
 $HO_2CCH_2SCH_2CH_2CO_2H$ , m.  $94^\circ$ ,<sup>172a, 176a, 286e, 375, 443</sup>  $93^\circ$ ; <sup>169</sup>  $K_1 2.3 \times 10^{-4}$ ,  $K_2 1.0 \times 10^{-4}$  at  $18^\circ$ ,<sup>276a</sup> K 0.025; <sup>286e, 287c</sup> diEt ester,  $b_3 121-3^\circ$ ,<sup>443</sup>  $b_8 136-8^\circ$ ,<sup>309b</sup>  $b_{10} 148-50^\circ$ ,<sup>202, 239</sup>  $b_{12} 154-5^\circ$ .<sup>61</sup>  
 $HO_2CCH_2SCH_2CH_2CO_2Et$ ,  $b_3 136-8^\circ$ .<sup>308</sup>  
 $EtO_2CCH_2SCH_2CH_2CO_2Me$ ,  $b_8 142^\circ$ ; d 20/4 1.146; n 20/D 1.4700.<sup>215</sup>  
 $HO_2CCH_2SCHMeCH_2CO_2H$ , m.  $45^\circ$ .<sup>274</sup>  
 $HO_2CCH_2SCH_2CHMeCO_2H$ , m.  $72^\circ$ ; <sup>270e</sup> mono Et ester,  $b_{13} 150-5^\circ$ ; <sup>149</sup> diEt ester, b.  $144^\circ$ .<sup>270e</sup>  
 $HO_2CCH_2SCH_2CHEtCO_2H$ ,  $b_{0.01} 70^\circ$ ; diEt ester,  $b_{11} 145-50^\circ$ .<sup>182</sup>  
 $EtO_2CCH_2SCHPhCH_2CO_2Et$ ,  $b_2 163-5^\circ$ .<sup>411</sup>

- $\text{HO}_2\text{CCHMeSCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $73^\circ$ ,<sup>286e</sup>  $70^\circ$ ; <sup>169</sup> K 0.021; <sup>286c</sup>,  
<sup>286e</sup>, <sup>287c</sup> diEt ester,  $b_{10.5}$   $149-53^\circ$ .<sup>239</sup>  
 $\text{HO}_2\text{CCMe}(\text{OH})\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $92^\circ$ .<sup>209a</sup>  
 $\text{HO}_2\text{CCMe}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $109^\circ$ ;  $K_1$   $1.3 \times 10^{-4}$  at  $25^\circ$ ,  $K_2$   
 $8.3 \times 10^{-4}$  at  $18^\circ$ .<sup>276a</sup>  
 $\text{HO}_2\text{CCMe}_2\text{SCH}_2\text{CHMeCO}_2\text{H}$ , m.  $153^\circ$ ;  $K_1$   $1.7 \times 10^{-4}$ ,  $K_2$   
 $7.6 \times 10^{-5}$  at  $18^\circ$ .<sup>276b</sup>  
 $\text{EtO}_2\text{CCHAmSCH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{0.02}$   $142^\circ$ .<sup>236</sup>  
 $\text{HO}_2\text{CCH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $75^\circ$ ; diEt ester,  $b_4$   $139-42^\circ$ .<sup>132</sup>  
 $\text{HO}_2\text{CCH}_2\text{CH}_2\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CH}_2\text{CH}_2\text{OPh}$ , m.  $90.5^\circ$ ; <sup>85b</sup>, <sup>86</sup>  
diMe ester,  $b_3$   $200-10^\circ$ ; n 20/D 1.5248; <sup>86</sup> diEt ester,  $b_3$   $200-5^\circ$ ;  
n 20/D 1.5120.<sup>85b</sup>, <sup>86</sup>  
 $\text{EtO}_2\text{CCH}_2\text{CH}_2\text{SCH}(\text{CO}_2\text{Et})\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}$ ,  $b_2$   $200-16^\circ$ ;  
n 20/D 1.5118.<sup>86</sup>  
 $\text{EtO}_2\text{CCH}_2\text{CH}_2\text{SCH}(\text{CO}_2\text{Et})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OMe}$ ,  $b_{0.02}$   $145-$   
 $8^\circ$ .<sup>372</sup>  
 $\text{MeO}_2\text{CCH}(\text{OMe})\text{CH}_2\text{SCH}(\text{CO}_2\text{Me})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OMe}$ ,  $b_{0.008}$   
 $140-5^\circ$ .<sup>372</sup>  
 $\text{HO}_2\text{CCH}_2\text{SCH}(\text{CH}_2\text{COPh})\text{CO}_2\text{H}$ , hydrate, m.  $75^\circ$ .<sup>51</sup>  
 $\text{EtO}_2\text{CCH}_2\text{CH}_2\text{SCH}(\text{CO}_2\text{Et})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$ ,  $b_{0.01}$   $162-$   
 $5^\circ$ .<sup>238</sup>  
 $\text{HO}_2\text{CCH}_2\text{SCMe}:\text{CHCO}_2\text{H}$ , m.  $203^\circ$  and  $161^\circ$ ; diMe ester,  $b_{12}$   
 $172-5^\circ$ ; diEt ester, m.  $45^\circ$ ;  $b_{10}$   $168-79^\circ$ ,<sup>369</sup>  $b_9$   $116^\circ$ .<sup>80</sup>  
 $\text{EtO}_2\text{CCHMeSCMe}:\text{CHCO}_2\text{Et}$ ,  $b_5$   $124^\circ$ .<sup>80</sup>  
 $o\text{-HO}_2\text{CCH}_2\text{SC}_6\text{H}_4\text{CO}_2\text{H}$ , m.  $213^\circ$ .<sup>157</sup>  
 $\text{HO}_2\text{CCH}_2\text{SCHPhNHC}_6\text{H}_4\text{CO}_2\text{H-}o$ , m.  $91^\circ$ .<sup>396</sup>  
 $\text{HO}_2\text{CCH}_2\text{CH}_2\text{SCHPhNHC}_6\text{H}_4\text{CO}_2\text{H-}o$ , m.  $116^\circ$ .<sup>396</sup>

### Tribasic Acids

- $\text{HO}_2\text{CCH}_2\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m.  $139^\circ$ ,<sup>271b</sup>  $140.5^\circ$ ; <sup>310a</sup> triEt  
ester,  $b_{0.8}$   $140-5^\circ$ ; d 25/4 1.1498; n 25/D 1.4646; triPr ester,  
 $b_{0.2}$   $125-31^\circ$ ; tri-*i*-Pr ester,  $b_{0.4}$   $124-9^\circ$ ; triBu ester,  $b_{0.2}$   $161-$   
 $3^\circ$ ; <sup>312</sup>  $b_{6.5}$   $214-6^\circ$ ; <sup>363</sup> d 25/4 1.0517, <sup>312</sup>  $d_{30}$  1.407; <sup>363</sup> n 25/D  
1.4606, <sup>312</sup> n 30/D 1.4591; <sup>363</sup> tri-*i*-Bu ester,  $b_{0.37}$   $167-9^\circ$ ; d 25/4  
1.042; n 25/D 1.4583; triHex ester,  $b_{0.4}$   $200-3^\circ$ ; d 25/4 1.013;  
n 25/D 1.4644;  $(\text{Et}_2\text{CHCH}_2\text{-ester})_3$ ,  $b_{0.4}$   $205-8^\circ$ ; d 25/4 1.012;  
n 25/D 1.4649;  $(\text{BuEtCHCH}_2\text{-ester})_3$ ,  $b_{0.37}$   $222-7^\circ$ ; d 25/4  
0.9801; n 25/D 1.4663; <sup>137</sup> tri-octadecyl ester, m.  $50^\circ$ ; <sup>312</sup> N-Et  
imide, m.  $91^\circ$ ; N-Ph imide, m.  $154.5^\circ$ .<sup>294</sup>  
 $\text{HO}_2\text{CCHMeSCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m.  $179^\circ$ .<sup>271b</sup>

$\text{HO}_2\text{CCMe}_2\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m.  $200^\circ$ .<sup>271b</sup>  
 $\text{HO}_2\text{CCH}_2\text{CH}_2\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m.  $155^\circ$ ,<sup>169</sup>  $151^\circ$ .<sup>271b</sup>  
 $\text{HO}_2\text{CCHMeCH}_2\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , m.  $184^\circ$ .<sup>271b</sup>  
 $\text{EtO}_2\text{CCH}_2\text{CH}_2\text{SCH}(\text{CO}_2\text{Et})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ ,  $b_{0.02}$   $150-3^\circ$ .<sup>236, 237</sup>  
 $\text{HO}_2\text{CCH}_2\text{SCH}(\text{CO}_2\text{H})\text{CH}_2(\text{CH}_2)_3\text{CO}_2\text{H}$ , triMe ester,  $b_1$   $192-5^\circ$ ,<sup>17, 18</sup>  $198^\circ$ ; <sup>60</sup> triEt ester,  $b_3$   $210-3^\circ$ .<sup>85a, 86</sup>  
 $o\text{-HO}_2\text{CC}_6\text{H}_4\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ , N-Et imide, m.  $163.5^\circ$ ;  
 N-Ph imide, m.  $180^\circ$ .<sup>294</sup>  
 $\text{EtO}_2\text{CCH}_2\text{SC}(\text{CH}_2\text{CO}_2\text{Et})\text{:CHCO}_2\text{Et}$ ,  $b_6$   $170^\circ$ .<sup>303b</sup>  
 $\text{EtO}_2\text{CCHMeSCMe:C}(\text{CO}_2\text{Et})_2$ ,  $b_5$   $125^\circ$ .<sup>80</sup>

### Tetra- and Hexabasic Acids

$\text{S}[\text{CH}(\text{CO}_2\text{H})_2]_2$ , tetraMe ester, m.  $122^\circ$ ;  $(-\text{CONHPr})_4$ , m.  $123^\circ$ ;  $(-\text{CONHi-Bu})_4$ , m.  $155^\circ$ .<sup>313</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}]_2$ , m.  $213^\circ$ ,<sup>316</sup>  $187^\circ$ .<sup>382</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{Me})\text{CH}_2\text{CO}_2\text{Me}]_2$ , m.  $42^\circ$ ;  $b_{0.5}$   $175^\circ$ ; d 20/4 1.2530; n 20/D 1.4779.<sup>316, 317</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{Et})\text{CH}_2\text{CO}_2\text{Et}]_2$ ,  $b_{5.5}$   $222^\circ$ ; d 20/4 1.1470; n 20/D 1.4643.<sup>316, 317</sup>  
 $\text{S}[\text{CH}(\text{CO}_2i\text{-Pr})\text{CH}_2\text{CO}_2i\text{-Pr}]_2$ ,  $b_{1.5}$   $185^\circ$ ; d 20/4 1.070; n 20/D 1.4538.<sup>316, 317</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{Bu})\text{CH}_2\text{CO}_2\text{Bu}]_2$ ,  $b_{0.05}$   $156^\circ$ ; d 20/4 1.0526; n 30/D 1.4589.<sup>316, 317</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{Hex})\text{CH}_2\text{CO}_2\text{Hex}]_2$ ,  $b_{0.025}$   $183^\circ$ ; d 20/4 1.0065; n 30/D 1.4596.<sup>316, 317</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{CH}_2\text{CHEt}_2)\text{CH}_2\text{CO}_2\text{CH}_2\text{CHEt}_2]_2$ ,  $b_{0.5}$   $231^\circ$ ; d 20/4 1.014; n 20/D 1.4654.<sup>316, 317</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{CH}_2\text{CHEtBu})\text{CH}_2\text{CO}_2\text{CH}_2\text{CHEtBu}]_2$ ,  $b_{0.017}$   $183^\circ$ ; d 20/4 0.9803; n 30/D 1.4610.<sup>316, 317</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{CH}_2\text{CHMe}(\text{CH}_2)_3\text{CHMe}_2)\text{CH}_2\text{CO}_2\text{CH}_2\text{CHMe}(\text{CH}_2)_3\text{CHMe}_2]_2$ ,  $b_{0.002}$   $156^\circ$ ; d 20/4 0.9403; n 30/D 1.4527.<sup>316, 317</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{CHMeCHEtHex})\text{CH}_2\text{CO}_2\text{CHMeCHEtHex}]_2$ ,  $b_{0.020}$   $207^\circ$ ; d 20/4 0.9533; n 32/D 1.4620.<sup>316</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{CH}_2\text{Ph})\text{CH}_2\text{CO}_2\text{CH}_2\text{Ph}]_2$ , m.  $49.4^\circ$ .<sup>317</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{CH}_2\text{CH:CH}_2)\text{CH}_2\text{CO}_2\text{CH}_2\text{CH:CH}_2]_2$ ,  $b_{0.4}$   $149^\circ$ ; d 20/4 1.147; n 20/D 1.4908.<sup>316</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{CH}_2\text{CH}_2\text{Cl})\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{Cl}]_2$ , m.  $84^\circ$ .<sup>316</sup>  
 $\text{S}[\text{CH}(\text{CO}_2\text{CH}_2\text{CH}_2\text{OMe})\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{OMe}]_2$ , m.  $42^\circ$ ;  $b_{0.2}$   $220^\circ$ .<sup>316, 317</sup>



$S[CH(CO_2CH_2CH_2OPh)CH_2CO_2CH_2CH_2OPh]_2$ , m.  $67^\circ$ .<sup>316, 317</sup>  
 $S[CMe(CO_2Bu)CH_2CO_2Bu]_2$ ,  $b_{1.5}$   $225^\circ$ ; d 20/4 1.044; n 20/D 1.4644.<sup>316, 317</sup>

$S[CH(CO_2Et)CH(CO_2Et)CH_2CO_2Et]_2$ ,  $b_{0.003}$   $171^\circ$ ; d 20/4 1.1579; n 20/D 1.4681.<sup>316, 317</sup>

$S[CH(CO_2Bu)CH(CO_2Bu)CH_2CO_2Bu]_2$ ,  $b_{0.005}$   $183^\circ$ ; d 20/4 1.0603; n 20.5/D 1.4645.<sup>316, 317</sup>

### Mercaptal Acids

$H_2C(SCH_2CO_2H)_2$ , m.  $129^\circ$ ,<sup>211, 270a</sup>  $127^\circ$ ; <sup>407a</sup> diEt ester,  $b_{14}$   $188-90^\circ$ ; <sup>205b</sup> dianilide, m.  $92^\circ$ .<sup>380a</sup>

$H_2C(SCHMeCO_2H)_2$ , DL- m.  $156^\circ$ ,<sup>146b</sup>  $152^\circ$ ; <sup>407a</sup> D- and L- m.  $83.5^\circ$ ; *meso*- m.  $82.5^\circ$ ; DL- solubility in water 3.35 g./l. at  $25^\circ$ ; DL- and *meso*,  $K$   $4.2 \times 10^{-4}$ .<sup>146b</sup>

$H_2C(SCH_2CH_2CO_2H)_2$ , m.  $143^\circ$ ,<sup>209a</sup>  $142^\circ$ ,<sup>407a</sup>  $141^\circ$ .<sup>169</sup>

$H_2C(SCH_2CH_2CH_2CO_2H)_2$ , m.  $120^\circ$ ; diBu ester,  $b_{0.5}$   $200^\circ$ .<sup>414</sup>

$MeCH(SCH_2CO_2H)_2$ , m.  $110^\circ$ ,<sup>205b</sup>  $108^\circ$ ; <sup>48b</sup> diEt ester,  $b_2$   $156-8^\circ$ ; <sup>205b</sup> *p*-aniside, m.  $168^\circ$ ; *p*-phenetide, m.  $171^\circ$ .<sup>28c</sup>

$MeCH(SCHMeCO_2H)_2$ , m.  $80^\circ$ .<sup>355</sup>

$MeCH(SCH_2CH_2CO_2H)_2$ , m.  $63^\circ$ .<sup>209a</sup>

$EtCH(SCH_2CO_2H)_2$ , m.  $75^\circ$ .<sup>205a</sup>

$EtCH(SCH_2CH_2CO_2H)_2$ , m.  $94.5^\circ$ .<sup>209a</sup>

$PrCH(SCH_2CO_2H)_2$ , m.  $63^\circ$ ; <sup>355</sup> anilide, m.  $75^\circ$ .<sup>380a</sup>

$PrCH(SCHMeCO_2H)_2$ , m.  $59^\circ$ .<sup>355</sup>

$C_6H_{13}CH(SCH_2CO_2H)_2$ , m.  $57^\circ$ .<sup>355</sup>

$C_6H_{13}CH(SCH_2CH_2CO_2H)_2$ , m.  $67^\circ$ .<sup>355</sup>

$PhCH(SCH_2CO_2H)_2$ , m.  $127^\circ$ ,<sup>205b, 211</sup>  $124^\circ$ .<sup>407a</sup>

$PhCH(SCHMeCO_2H)_2$ , m.  $140^\circ$ ,<sup>211</sup>  $150^\circ$ .<sup>407a</sup>

$PhCH(SCH_2CH_2CO_2H)_2$ , m.  $90^\circ$ ,<sup>407a</sup>  $89^\circ$ .<sup>209a</sup>

$PhCH_2CH(SCH_2CO_2H)_2$ , m.  $100^\circ$ .<sup>205c</sup>

$PhCH_2CH(SCH_2CH_2CO_2H)_2$ , m.  $110^\circ$ .<sup>209a</sup>

$PhCH_2CH_2CH(SCH_2CO_2H)_2$ , m.  $111^\circ$ .<sup>205c</sup>

$PhCH_2CH_2CH(SCH_2CH_2CO_2H)_2$ , m.  $73^\circ$ .<sup>209a</sup>

$PhCH:CHCH(SCH_2CH_2CO_2H)_2$ , m.  $95^\circ$ .<sup>209a</sup>

2- $C_4H_9S\cdot CH(SCH_2CH_2CO_2H)_2$ , m.  $88^\circ$ .<sup>209a</sup>

*p*- $MeOC_6H_4CH(SCH_2CO_2H)_2$ , m.  $122.5^\circ$ .<sup>355</sup>

*p*- $MeOC_6H_4CH(SCHMeCO_2H)_2$ , m.  $141^\circ$ .<sup>355</sup>

*p*- $MeOC_6H_4CH(SCH_2CH_2CO_2H)_2$ , m.  $110.5^\circ$ .<sup>355</sup>

3,4- $MeO(HO)C_6H_3CH(SCH_2CO_2H)_2$ , m.  $135^\circ$ ,<sup>355</sup>  $138^\circ$ ,<sup>205c</sup>  $137^\circ$ .<sup>205b</sup>

3,4-MeO(HO)C<sub>6</sub>H<sub>3</sub>CH(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 124°. <sup>209a</sup>  
 2,3-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 135°. <sup>355</sup>  
 2,3-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 100°. <sup>355</sup>  
 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 122°, <sup>355</sup> 126°. <sup>205c</sup>  
 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 89°. <sup>209a</sup>  
 3,4-CH<sub>2</sub>(O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 135.5°. <sup>355</sup>  
 3,4-CH<sub>2</sub>(O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH(SCHMeCO<sub>2</sub>H)<sub>2</sub>, m. 130°. <sup>355</sup>  
 C<sub>4</sub>H<sub>3</sub>O-CH(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 105°, <sup>48b</sup> 109°. <sup>205b</sup>  
 HO<sub>2</sub>CCH(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 132°. <sup>209a</sup>  
 [CH(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>]<sub>2</sub>, m. 189°. <sup>355</sup>  
 [CH(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>]<sub>2</sub>, m. 162°. <sup>355</sup>

### Mercaptole Acids

Me<sub>2</sub>C(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 135°, <sup>48a</sup>, <sup>385</sup> 127°, <sup>48b</sup> 129°; <sup>407a</sup> diEt ester,  
 b<sub>1.8</sub> 152-3°; d 20/4 1.1350; n 20/D 1.4070; <sup>385</sup> dianilide, m.  
 170°. <sup>28a</sup>  
 Me<sub>2</sub>C(SCHMeCO<sub>2</sub>H)<sub>2</sub>, m. 174°, <sup>407a</sup> 171°. <sup>355</sup>  
 Me<sub>2</sub>C(SCHEtCO<sub>2</sub>H)<sub>2</sub>, *p*-toluide, m. 155°. <sup>28e</sup>  
 Me<sub>2</sub>C(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 70°, <sup>407a</sup> 89°. <sup>209a</sup>  
 MeEtC(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 111°, <sup>205c</sup> 107.5°. <sup>355</sup>  
 MeEtC(SCHMeCO<sub>2</sub>H)<sub>2</sub>, m. 127°. <sup>355</sup>, <sup>407a</sup>  
 MeEtC(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 54°. <sup>209a</sup>  
 MePrC(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 113°. <sup>209c</sup>  
 Me(*i*-Bu)C(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 85°. <sup>355</sup>  
 Me(*i*-Bu)C(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 101.5°. <sup>355</sup>  
 MeAmC(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 75°. <sup>355</sup>  
 MeAmC(SCHMeCO<sub>2</sub>H)<sub>2</sub>, m. 123°. <sup>355</sup>  
 MeAmC(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 89°. <sup>355</sup>  
 Et<sub>2</sub>C(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 126°, <sup>385</sup> 126.5°; <sup>209c</sup> diEt ester, b<sub>2</sub> 162-3°;  
 d 20/4 1.1120; n 20/D 1.4969. <sup>385</sup>  
 Et<sub>2</sub>C(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 98°. <sup>209a</sup>  
 Pr<sub>2</sub>C(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 134°; diEt ester, b<sub>3</sub> 178-9°; d 20/4  
 1.0740; n 20/D 1.4709. <sup>385</sup>  
 Bu<sub>2</sub>C(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 87°; diEt ester, b<sub>3</sub> 183-4°; d 20/4 1.0251;  
 n 20/D 1.4862. <sup>385</sup>  
 (C<sub>6</sub>H<sub>13</sub>)<sub>2</sub>C(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 85°. <sup>355</sup>  
 (C<sub>6</sub>H<sub>13</sub>)<sub>2</sub>C(SCHMeCO<sub>2</sub>H)<sub>2</sub>, m. 114°. <sup>355</sup>  
 C<sub>6</sub>H<sub>10</sub>(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 140°, <sup>205c</sup> 132°. <sup>355</sup>  
 C<sub>6</sub>H<sub>10</sub>(SCHMeCO<sub>2</sub>H)<sub>2</sub>, m. 126°. <sup>355</sup>  
 C<sub>6</sub>H<sub>10</sub>(SCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 97°. <sup>209a</sup>

$\text{MePhC}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $135^\circ$ .<sup>210</sup>  
 $\text{MePhC}(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $112^\circ$ .<sup>209a</sup>  
 $\text{MePhCH}_2\text{C}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $130^\circ$ .<sup>209c</sup>  
 $\text{MePhCH}_2\text{C}(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $118^\circ$ .<sup>209a</sup>  
 $\text{Me}(p\text{-HOC}_6\text{H}_4)\text{C}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $122^\circ$  with decomposition.<sup>355</sup>  
 $\text{Me}(p\text{-PhC}_6\text{H}_4)_2\text{C}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $172^\circ$  with decomposition.<sup>355</sup>  
 $\text{PrPhC}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $156^\circ$ .<sup>355</sup>  
 $\text{PrPhC}(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $104$ .<sup>355</sup>  
 $\text{Ph}_2\text{C}(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $148.5^\circ$ .<sup>209a</sup>  
 $\text{CH}_2[\text{CMe}(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2]_2$ , m.  $121^\circ$  with decomposition.<sup>355</sup>  
 $[\cdot\text{CH}_2\text{CMe}(\text{SCH}_2\text{CO}_2\text{H})_2]_2$ , m.  $166^\circ$ .<sup>354</sup>  
 $[\cdot\text{CH}_2\text{CMe}(\text{SCHMeCO}_2\text{H})_2]_2$ , m.  $190^\circ$  with decomposition.<sup>355</sup>  
 $[\cdot\text{CH}_2\text{CMe}(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2]_2$ , m.  $175^\circ$  with decomposition.<sup>355</sup>

### Mercaptals and Mercaptoles of Acids

$(\text{MeS})_2\text{CHCO}_2\text{H}$ , m.  $79^\circ$ ; <sup>415</sup> Et ester,  $b_{12}$   $115-7^\circ$ .<sup>46</sup>  
 $(\text{EtS})_2\text{CHCO}_2\text{Et}$ ,  $b_{12}$   $130-3^\circ$ .<sup>46</sup>  
 $(\text{BuS})_2\text{CHCONH}_2$ , m.  $105^\circ$ .<sup>117</sup>  
 $(\text{PhCH}_2\text{S})_2\text{CHCO}_2\text{H}$ , m.  $112^\circ$ .<sup>415</sup>  
 $(\text{PhCH:CHS})_2\text{CHCO}_2\text{H}$ , m.  $115^\circ$ .<sup>210</sup>  
 $(p\text{-NH}_2\text{C}_6\text{H}_4\text{S})_2\text{CHCOOH}$ , m.  $119^\circ$ , diAc., m.  $230-5^\circ$ .<sup>38</sup>  
 $(\text{EtS})_2\text{CMeCO}_2\text{H}$ , m.  $60^\circ$ ,<sup>128</sup>  $62^\circ$ ; <sup>335a</sup>  $\text{NH}_4$  salt, m.  $176^\circ$ .<sup>55</sup>  
 $(\text{PhS})_2\text{CMeCO}_2\text{H}$ , m.  $117^\circ$ , amide, m.  $93^\circ$ .<sup>128</sup>  
 $(\text{PhCH}_2\text{S})_2\text{CMeCO}_2\text{H}$ , m.  $100^\circ$ .<sup>335b</sup>  
 $(\text{PhS})_2\text{CPhCO}_2\text{H}$ , m.  $143^\circ$ .<sup>128</sup>  
 $(\text{BuS})_2\text{CHCH}_2\text{CO}_2\text{Et}$ ,  $b_1$   $138-43^\circ$ ;  $n$  20/D 1.4866.<sup>99</sup>  
 $(\text{OctS})_2\text{CHCH}_2\text{CO}_2\text{Et}$ ,  $b_{0.15}$   $176-97^\circ$ ;  $n$  20/D 1.4820.<sup>99</sup>  
 $(\text{EtS})_2\text{CMeCH}_2\text{CO}_2\text{Et}$ ,  $b_{37}$   $137-8^\circ$ ;  $d$  16/16 1.0341.<sup>335a</sup>  
 $(\text{PhS})_2\text{CMeCH}_2\text{CO}_2\text{H}$ , m.  $58^\circ$ .<sup>128</sup>  
 $(\text{EtS})_2\text{CMeCHMeCO}_2\text{Et}$ ,  $b_{29}$   $125^\circ$ ,  $b_{39}$   $132^\circ$ ;  $d$  15/4 1.0575;  $n$  15/D 1.51326.<sup>335a</sup>  
 $(\text{EtS})_2\text{CMeCHEtCO}_2\text{Et}$ ,  $b_{39}$   $138^\circ$ ,  $b_{49}$   $152^\circ$ ;  $d$  16/4 1.0071;  $n$  15/D 1.49394.<sup>335a</sup>  
 $(\text{PhS})_2\text{CMeCH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $69^\circ$ .<sup>128</sup>  
 $(\text{EtS})_2\text{C}(\text{COMe})\text{CO}_2\text{Et}$ ,  $b_{14}$   $164^\circ$ .<sup>56</sup>  
 $(\text{EtS})_2\text{C}(\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $141^\circ$ ; diEt ester,  $b_{30}$   $192^\circ$ ;  $d$  17/4 1.1006;  $n$  25/D 1.5051.<sup>335a</sup>  
 $\text{Me}(\text{HO}_2\text{C})\text{C}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $165^\circ$ ,<sup>205c</sup>  $162^\circ$ ,<sup>48b</sup>  $160^\circ$ .<sup>48a</sup>  
 $\text{Me}(\text{HO}_2\text{CCH}_2)\text{C}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $147^\circ$ .<sup>205c</sup>

- $\text{Me}(\text{EtO}_2\text{CCH}_2)\text{C}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $96^\circ$ ; <sup>48b</sup> triEt ester, m.  $101^\circ$ .<sup>205c</sup>  
 $\text{Me}(\text{EtO}_2\text{CCH}_2)\text{C}(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $130^\circ$ .<sup>209a</sup>  
 $\text{Me}(\text{HO}_2\text{CCH}_2\text{CH}_2)\text{C}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $154^\circ$ .<sup>48b</sup>  
 $\text{Me}(\text{HO}_2\text{CCH}_2\text{CH}_2)\text{C}(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $143^\circ$ .<sup>209a</sup>  
 $\text{Ph}(\text{HO}_2\text{C})\text{C}(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $162^\circ$ .<sup>209a</sup>  
 $\text{Ph}(\text{HO}_2\text{CCH}_2\text{SCH}_2)\text{C}(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $150^\circ$ .<sup>206a</sup>  
 $(\text{MeS})_2\text{C}:\text{CHCO}_2\text{H}$ , m.  $197^\circ$ ; <sup>241</sup>  $97^\circ$ ; <sup>240</sup> Et ester, m.  $56^\circ$ ; <sup>240</sup>, <sup>207</sup>  $b_{15}$   $164^\circ$ .<sup>240</sup>, <sup>241</sup>  
 $(\cdot\text{CH}_2\text{S})_2\text{C}:\text{CHCO}_2\text{H}$ , m.  $150^\circ$ .<sup>240</sup>  
 $(\text{MeS})_2\text{C}:\text{C}(\text{CN})\text{CO}_2\text{Et}$ , m.  $57^\circ$ ; <sup>240</sup>, <sup>241</sup>  $b_{30}$   $215^\circ$ .<sup>240</sup>  
 $(\text{EtS})_2\text{C}:\text{C}(\text{CN})\text{CO}_2\text{Et}$ , m.  $84^\circ$ ; <sup>240</sup>  $b_{1.5}$   $180^\circ$ .<sup>241</sup>  
 $(\text{PhCH}_2\text{S})_2\text{C}:\text{C}(\text{CN})\text{CO}_2\text{Et}$ , m.  $84^\circ$ .<sup>241</sup>  
 $\text{CH}_2(\text{CH}_2\text{S})_2\text{C}:\text{C}(\text{CN})\text{CO}_2\text{Et}$ , m.  $92^\circ$ .<sup>240</sup>  
 $(\text{MeS})_2\text{C}:\text{C}(\text{CO}_2\text{Et})_2$ ,  $b_{15}$   $196^\circ$ .<sup>240</sup>, <sup>241</sup>  
 $(\cdot\text{CH}_2\text{S})_2\text{C}:\text{C}(\text{CO}_2\text{Et})_2$ ,  $b_{2.5}$   $202^\circ$ .<sup>240</sup>  
 $\text{CH}_2(\text{CH}_2\text{S})_2\text{C}:\text{C}(\text{COOH})_2$ , m.  $215^\circ$  with decomposition.<sup>240</sup>

### Other bis-Sulfide Acids

- $\text{PhSCH}_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H}$ , m.  $51^\circ$ .<sup>143</sup>  
 $\text{PhSO}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H}$ , m.  $84^\circ$ .<sup>144</sup>  
 $\text{PhSCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H}$ , m.  $79^\circ$ .<sup>143</sup>  
 $(\text{MeSCH}_2)_2\text{CHCO}_2\text{H}$ , m.  $25^\circ$ .<sup>229</sup>, <sup>230</sup>  
 $\text{PhCH}_2\text{SCH}_2\text{CH}_2\text{CH}(\text{SCH}_2\text{Ph})\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , m.  $69^\circ$ ; <sup>349</sup>  $65^\circ$ .<sup>393</sup>  
 $(\cdot\text{CH}_2\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $109^\circ$ ; <sup>270a</sup>, <sup>344</sup>  $108.5^\circ$ ; <sup>169</sup>  $108^\circ$ ; <sup>12</sup>, <sup>353b</sup>  $107^\circ$ ; <sup>88</sup>  $105^\circ$ ; <sup>157</sup> diMe ester,  $b_{11}$   $190^\circ$ ;  $d_{25}$  1.2332;  $n_{25/D}$  1.524; diEt ester,  $b_{11}$   $198^\circ$ ;  $d_{25}$  1.1609;  $n_{25/D}$  1.510; diamide, m.  $175.5^\circ$ ; <sup>422a</sup> dianilide, m.  $158^\circ$ ; <sup>28b</sup> di-*p*-aniside, m.  $178^\circ$ ; di-*p*-phenetide, m.  $197^\circ$ ; <sup>28d</sup> di-*p*-toluide, m.  $205^\circ$ .<sup>422a</sup>  
 $(\cdot\text{CH}_2\text{SCHMeCO}_2\text{H})_2$ , DL- m.  $90^\circ$ ; *meso*- m.  $118^\circ$ ; <sup>353b</sup> dianilide, m.  $174^\circ$ .<sup>28b</sup>  
 $(\cdot\text{CH}_2\text{SCHEtCO}_2\text{H})_2$ , dianilide, m.  $125^\circ$ ; <sup>28b</sup> di-*p*-toluide, m.  $202^\circ$ .<sup>28e</sup>  
 $(\cdot\text{CH}_2\text{SCHPhCO}_2\text{H})_2$ , DL- m.  $128^\circ$ ; *meso*- m.  $158^\circ$ .<sup>353b</sup>  
 $(\cdot\text{CH}_2\text{SCMe}_2\text{CO}_2\text{H})_2$ , m.  $168^\circ$ .<sup>353b</sup>  
 $\text{CH}_2(\text{CH}_2\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $72^\circ$ ; <sup>270a</sup>  $71.6^\circ$ ; <sup>360</sup>  $71.5^\circ$ ; <sup>169</sup>  $b_{15}$   $207-8^\circ$ ;  $d_{19}$  1.492 solid; diMe ester,  $b_{15}$   $207-8^\circ$ ;  $d_{16/4}$  1.210; diEt ester,  $b_{23}$   $224-5^\circ$ ;  $d_{16/4}$  1.143; diamide, m.  $127^\circ$ ; <sup>360</sup> dianilide, m.  $155^\circ$ ; <sup>28b</sup> di-*p*-aniside, m.  $139^\circ$ ; di-*p*-phenetide, m.  $147^\circ$ .<sup>28d</sup>

- $(\cdot\text{CH}_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $122^\circ$ ,<sup>270a</sup>  $121^\circ$ .<sup>394</sup>  
 $\text{CH}_2(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $94^\circ$ ,<sup>270a</sup>  $92^\circ$ .<sup>88</sup>  
 $(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $119^\circ$ .<sup>270a</sup>  
 $(\cdot\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $159.5^\circ$ ,<sup>353c</sup>  $159^\circ$ ,<sup>169</sup>  $153^\circ$ ,<sup>105</sup>  $148^\circ$ ; <sup>249</sup>  
 diMe ester, m.  $30.5^\circ$ ;  $b_{0.5}$   $177^\circ$ ;  $n$  31/D  $1.5062$ .<sup>106</sup>  
 $\text{CH}_2(\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $110.5^\circ$ ,<sup>169</sup>  $109^\circ$ .<sup>275</sup>  
 $(\cdot\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $108^\circ$ .<sup>169, 275</sup>  
 $\text{CH}_2(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $110.5^\circ$ ,<sup>169</sup>  $110^\circ$ .<sup>275</sup>  
 $(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $116.5^\circ$ .<sup>169</sup>  
 $\text{HO}_2\text{CCH}_2\text{SCH}_2\text{CHMeSCH}_2\text{CO}_2\text{H}$ , m.  $35^\circ$ ; <sup>353a</sup> *p*-aniside, m.  $103^\circ$ ; *p*-phenetide, m.  $158^\circ$ .<sup>28d</sup>  
 $\text{HO}_2\text{CCH}_2\text{SCH}_2\text{CHPhSCH}_2\text{CO}_2\text{H}$ , m.  $86^\circ$ ; <sup>206d</sup> diEt ester,  $b_3$   $210-12^\circ$ .<sup>207b</sup>  
 $\text{HO}_2\text{CCH}_2\text{SCPh:CPHSCCH}_2\text{CO}_2\text{H}$ , m.  $213^\circ$ ; diMe ester, m.  $98^\circ$ .<sup>31</sup>  
 $m\text{-C}_6\text{H}_4(\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $121^\circ$ .<sup>154a</sup>  
 $2,5\text{-Cl}_2\text{C}_6\text{H}_2(\text{SCH}_2\text{CO}_2\text{H})_{2-1,3}$ , m.  $190^\circ$ .<sup>159</sup>  
 $4,6\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_4(\text{SCH}_2\text{CO}_2\text{H})_{2-1,3}$ , m.  $236^\circ$ ;  $(\text{---COCl})_2$ , m.  $106^\circ$   
 with decomposition; diamide, m.  $223^\circ$ ; diMe ester, m.  $150^\circ$ ;  
 diEt ester, m.  $126^\circ$ .<sup>139</sup>  
 $o,o'\text{-(}\cdot\text{C}_6\text{H}_4\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $202^\circ$ .<sup>21</sup>  
 $m\text{-C}_6\text{H}_4(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $124^\circ$ ,<sup>138</sup>  $123^\circ$ .<sup>172a</sup>  
 $p\text{-C}_6\text{H}_4(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $181^\circ$ .<sup>35</sup>  
 $4\text{-O}_2\text{NC}_6\text{H}_4(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_{2-1,3}$ , m.  $157^\circ$ .<sup>138</sup>  
 $4\text{-H}_2\text{NC}_6\text{H}_4(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_{2-1,3}$ , m.  $122^\circ$ ; HCl m.  $187^\circ$ .<sup>138</sup>  
 $4,6\text{-Br}_2\text{C}_6\text{H}_2(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_{2-1,3}$ , m.  $184^\circ$ .<sup>138</sup>  
 $1,5\text{-C}_{10}\text{H}_6(\text{CH}_2\text{SCH}_2\text{CO}_2\text{H})_2$ , m.  $153^\circ$ .<sup>192</sup>  
 $m\text{-C}_6\text{H}_4(\text{SC}_6\text{H}_4\text{CO}_2\text{H})_2$ , m.  $303^\circ$ .<sup>388</sup>  
 $[\cdot\text{CH}_2\text{CH}(\text{SMe})\text{CO}_2\text{H}]_2$ , *meso*- m.  $193^\circ$ ; solubility in water at  
 $25^\circ$   $0.3$  g/l.; DL- m.  $124^\circ$ ; solubility in water  $1.57$  g/l.<sup>146c, 147c</sup>  
 $[\cdot\text{CH}_2\text{CH}(\text{SEt})\text{CO}_2\text{H}]_2$ , *meso*- m.  $171^\circ$ ; solubility in water  $0.3$   
 g/l.; DL- m.  $109.5^\circ$ ; solubility in water  $0.32$  g/l.<sup>146c, 147c</sup>  
 $[\cdot\text{CH}_2\text{CH}(\text{SC}_3\text{H}_5)\text{CO}_2\text{H}]_2$ , *meso*- m.  $121^\circ$ ; solubility in water  
 $0.94$  g/l.; DL- m.  $102^\circ$ ; solubility in water  $1.66$  g/l.<sup>146c, 147c</sup>  
 $[\cdot\text{CH}_2\text{CH}(\text{SCH}_2\text{Ph})\text{CO}_2\text{H}]_2$ , *meso*- m.  $169^\circ$ ; DL- m.  $130$ .<sup>146c, 147c</sup>  
 $[\cdot\text{CH}_2\text{CH}(\text{SCH}_2\text{CO}_2\text{H})\text{CO}_2\text{H}]_2$ , *meso*- m.  $177^\circ$ ; DL- m.  $162.5^\circ$ .<sup>146c, 147c</sup>  
 $\text{O}(\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $141^\circ$ .<sup>168</sup>  
 $\text{O}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $124.5^\circ$ ,<sup>169</sup>  $127^\circ$ .<sup>168</sup>  
 $\text{O}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $81^\circ$ ,<sup>169</sup>  $84.5^\circ$ .<sup>168</sup>  
 $(\cdot\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , m.  $97^\circ$ .<sup>168, 169</sup>

**tris-Sulfide Acids**

HC(SCH<sub>2</sub>CO<sub>2</sub>H)<sub>3</sub>, m. 171°, <sup>214</sup> 173°. <sup>211</sup>

**Some Selenide Acids**

PhSeCH<sub>2</sub>CO<sub>2</sub>H, m. 37°; b<sub>10</sub> 197–8°. <sup>122</sup>

MeC<sub>6</sub>H<sub>4</sub>SeCH<sub>2</sub>CO<sub>2</sub>H, *o*, m. 71°; *p*, m. 98°. <sup>30</sup>

O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SeCH<sub>2</sub>CO<sub>2</sub>H, *o*, m. 165°; *m*, m. 91°; *p*, m. 120°. <sup>30</sup>

ClC<sub>6</sub>H<sub>4</sub>SeCH<sub>2</sub>CO<sub>2</sub>H, *o*, m. 99°; *p*, m. 114°. <sup>30</sup>

H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SeCH<sub>2</sub>CO<sub>2</sub>H, *o* anhydride, m. 182°; *p*, m. 156°. <sup>30</sup>

MeOC<sub>6</sub>H<sub>4</sub>SeCH<sub>2</sub>CO<sub>2</sub>H, *o*, m. 87°; *p*, m. 70°. <sup>30</sup>

MeSC<sub>6</sub>H<sub>4</sub>SeCH<sub>2</sub>CO<sub>2</sub>H, *p*, m. 76°. <sup>30</sup>

Se(CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 109°, <sup>147b</sup> 108°; <sup>325</sup> K<sub>1</sub> 4.4 × 10<sup>-4</sup>, K<sub>2</sub> 0.339 × 10<sup>-4</sup>. <sup>147b</sup>

Se(CHMeCO<sub>2</sub>H)<sub>2</sub>, DL- m. 148°, <sup>147b</sup> 147°; <sup>146a</sup> K<sub>1</sub> 4.47 × 10<sup>-4</sup>, K<sub>2</sub> 0.219 × 10<sup>-4</sup>; <sup>147b</sup> D- and L- m. 124.5°, <sup>147b</sup> 124°; [α] 25/D 237.7° and -238.6°; <sup>146a</sup> *meso*- m. 129°; K<sub>1</sub> 3.80 × 10<sup>-4</sup>, K<sub>2</sub> 0.309 × 10<sup>-4</sup>. <sup>147b</sup>

Se(ChEtCO<sub>2</sub>H)<sub>2</sub>, DL- m. 101°; K<sub>1</sub> 4.11 × 10<sup>-4</sup>, K<sub>2</sub> 0.326 × 10<sup>-4</sup>; D- m. 77°; *meso*- m. 85°; K<sub>1</sub> 3.72 × 10<sup>-4</sup>, K<sub>2</sub> 0.328 × 10<sup>-4</sup>. <sup>147b</sup>

Se(CHPhCO<sub>2</sub>H)<sub>2</sub>, DL- m. 155°; D- m. 145°, K<sub>1</sub> 15.8 × 10<sup>-4</sup>, K<sub>2</sub> 0.906 × 10<sup>-4</sup>, L- m. 145°; *meso*- m. 179°, K<sub>1</sub> 15.0 × 10<sup>-4</sup>, K<sub>2</sub> 0.886 × 10<sup>-4</sup>. <sup>147b</sup>

Se(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 148°; <sup>147b</sup>, <sup>325</sup> K<sub>1</sub> 0.934 × 10<sup>-4</sup>, K<sub>2</sub> 0.156 × 10<sup>-4</sup>. <sup>147b</sup>

Se(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>, m. 96°. <sup>148</sup>

HO<sub>2</sub>CCMe<sub>2</sub>SeCH<sub>2</sub>CHMeCO<sub>2</sub>H, m. 155°; K<sub>1</sub> 1.20 × 10<sup>-4</sup>, K<sub>2</sub> 0.111 × 10<sup>-4</sup>. <sup>147b</sup>

MeSeC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, *m*, m. 121°; *p*, m. 175°, <sup>20</sup> 174°. <sup>158</sup>

PhSeC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, *p*, m. 184°. <sup>158</sup>

*p*-HO<sub>2</sub>CCH<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>SeCH<sub>2</sub>CO<sub>2</sub>H, m. 205°. <sup>30</sup>

Se(C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-*o*)<sub>2</sub>, m. 295°. <sup>358</sup>

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## CHAPTER 4.

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# Methionine

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It is remarkable that methionine, which was discovered as late as 1921, has been found to be so important. In this short time it has been the subject of hundreds of investigations. The space available here will be devoted to its chemistry; some articles of physiological interest only will be simply listed. Methionine has been ably reviewed by Toennies<sup>722a</sup> and has been included in a number of reviews on aminoacids.<sup>191, 222, 282c, 453b, 503b, 614a, 614b, 614c, 614d, 630b, 696, 722e, 745, 791c</sup>

Credit for the discovery of methionine goes to Mueller who isolated it from the hydrolysis products of casein.<sup>541a</sup> Previously, there had been observations of sulfur-containing protein products which were not cystine. These clues might have led to methionine had they been followed.<sup>244, 419, 531, 549, 560</sup>

### Occurrence of Methionine

Where there is protein, there is methionine. This general statement is believed to be true though it is based on the negative evidence that no protein that has been examined for methionine has been found not to contain it. Its presence has been demonstrated in scores of proteins of all classes. A few examples are taken from the extensive table compiled by Toennies.<sup>722a</sup> The figures are for percentage of methionine and for the fraction of the total sulfur accounted for by it.

TABLE 1.4  
*Methionine in Proteins*

Plant proteins	Methionine	Fraction of S
Arachin (peanut)	0.54%	28%
Edestin (hemp)	2.07	45
Gliadin	2.03	44
Sativin	3.93	52
$\alpha$ -Globulin (tomato seed)	3.14	70
Zein	2.58	51
Animal proteins		
Ovalbumin	5.24	70
Vitellin	2.70	51
Fibrin	2.59	57
Gelatin	0.97	44
Insulin	0.7	5
Wool	0.5	3
Casein	3.31	89
Lactalbumin	2.45	36

Commercial yeasts contain from 0.48 to 0.75% of methionine on dry basis.<sup>163,5</sup> The plant proteins shown in Toennies' large table average about 2% of methionine, the lowest being around 0.5% and the highest somewhat above 3%. The methionine usually accounts for about half of the total sulfur, though this may be as low as one-fourth or as high as three-fourths. Cystine accounts for most of the remaining sulfur. The methionine content of animal proteins is somewhat higher, averaging about 2.6% which, as in plants, represents about half of the total sulfur. The fraction of the total sulfur represented by methionine varies more widely, from 3% in wool to 90% in casein. Later information has been given on the methionine content of vegetable proteins.<sup>558</sup> Calculations of minimum molecular weights of biological materials have been based on their methionine content.<sup>139, 248, 455b</sup>

There has been such a multitude of investigations on the occurrence of methionine that it is impossible to go into any detail. References to some of these are given.<sup>1, 3, 20, 41, 43, 44, 51, 52b, 60, 61, 62, 63, 86, 90, 91, 100, 104b, 106, 107, 118b, 123, 126, 137, 146, 147, 166,</sup>

189, 203b, 205, 220, 232a, 233b, 234, 241, 246, 250, 254, 255, 258, 271, 282b, 292, 293, 294, 295, 311, 346, 347d, 352, 353, 366, 374, 375, 376, 393a, 395, 403, 407, 410a, 412, 432, 446, 447, 455a, 465a, 466, 467, 470, 479, 482, 494, 506, 516, 517, 543, 544, 557, 583, 584, 607, 626, 640, 647, 653, 654, 656, 657, 660, 668, 693, 697b, 720, 726, 727, 728, 763, 769, 803, 812, 829

It has been suggested that methionine may be a precursor of natural penicillins.<sup>71</sup>

The isolation of methionine is a tedious process, based largely on the precipitation, solution, and reprecipitation of complexes of mercury salts.<sup>1, 48, 224, 350a, 388, 541b, 541c, 556.5, 557, 581a, 581b, 581c, 665, 735.5, 762a</sup>

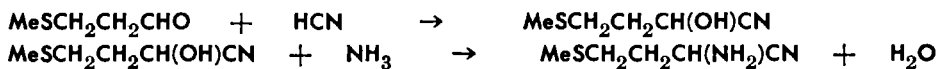
The details have been given fully by Toennies<sup>722a</sup> and need not be repeated here. An ionophoretic separation has been devised.<sup>590</sup>

### Synthesis

The first synthesis, one which confirmed the proposed structural formula, was by Barger and Coyne.<sup>48</sup> They started with the acetal of  $\beta$ -chloropropionaldehyde and methyl mercaptan:



The acetal was hydrolyzed and the resulting aldehyde combined with hydrocyanic acid in the presence of ammonium chloride:



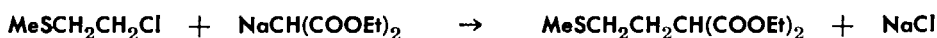
This was hydrolyzed to the acid,  $\text{MeSCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , which proved to be identical with the natural product, isolated from casein, except for the lack of optical activity.<sup>48, 510c</sup> The yield was low.

The synthesis of the  $\beta$ -methylmercaptopropionaldehyde has been accomplished more directly by the addition of methyl mercaptan to acrolein: <sup>150, 207.5, 272, 296, 456, 579</sup>



The  $\alpha$ -amino- $\gamma$ -(methylmercapto)butyronitrile may be converted to 5-( $\beta$ -methylmercaptoethyl)-dithiohydantoin by treatment with carbon disulfide<sup>150</sup> or to the corresponding hydantoin.<sup>272, 302.5, 579, 825.5</sup> Either of these can be hydrolyzed to DL-methionine.<sup>510b</sup> Recently, a careful study has been made of each of the steps in this synthesis with the result that the over-all yield has been improved greatly.<sup>356</sup>

A second synthesis started with  $\beta$ -methylmercaptoethyl chloride and malonic ester:

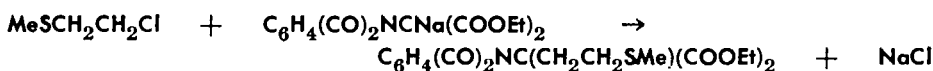


This was brominated and converted to the  $\alpha$ -amino- $\alpha$ -(methylmercaptoethyl)malonic acid which was decarboxylated to inactive methionine.<sup>229, 808a</sup> Cyanoacetic ester may be substituted for the malonic.<sup>267, 628</sup> Or the amino-group can be introduced into the malonic,<sup>230, 281, 732</sup> or cyanoacetic ester,<sup>13, 14, 223, 811</sup> and the acetylamino ester caused to react with the methylmercaptoethyl chloride:



A recent synthesis starts with  $\beta$ -methylmercaptoethyl chloride and acetoacetic ester which give the ester,  $\text{MeSCH}_2\text{CH}_2\text{CH}(\text{COMe})\text{CO}_2\text{Et}$ . This is treated with sodium and then with benzenediazonium chloride to make  $\text{MeSCH}_2\text{CH}_2\text{C}(:\text{NNHPh})\text{CO}_2\text{H}$  which can be reduced by zinc dust to methionine.<sup>239</sup>

Another approach is by way of ethyl phthalimidomalonate, which reacts with methylmercaptoethyl chloride, in the presence of sodium ethylate:



Hydrolysis of this gives racemic methionine.<sup>49a, 49b, 110</sup> Naphthalimidomalonate may be substituted for the phthalimidomalonate.<sup>492</sup> The methionine made by this method contains bimethionine,  $[\cdot\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}]_2$ , as an impurity. This has been synthesized by the use of  $(\cdot\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl})_2$  instead of the  $\text{MeSCH}_2\text{CH}_2\text{Cl}$ .<sup>665, 666</sup> Hydrogenolysis of bimethionine by Raney nickel gives two-thirds of the calculated ethane, the rest going on to methane.<sup>663</sup>

Several syntheses which differ in their latter steps, start with  $\gamma$ -butyrolactone. Bromination converts this to  $\alpha,\gamma$ -dibromobutyric acid, which on distillation loses hydrobromic acid to give the  $\alpha$ -bromolactone. This is treated, in succession, with ammonia and benzoyl chloride. The resulting  $\alpha$ -benzamido- $\gamma$ -butyrolactone, heated with alcohol and hydrogen chloride, gives ethyl  $\alpha$ -benzamido- $\gamma$ -chlorobutyrate which is made to react with sodium methyl mercaptide, or selenide, and then hydrolyzed to racemic methionine<sup>350b</sup> or selenomethionine.<sup>582</sup>



$\alpha$ -Aminobutyrolactone is heated with sodium methyl mercaptide to produce methionine.<sup>413b</sup>  $\alpha$ -Acetaminobutyrolactone is converted into 3,6-bis(2-hydroxyethyl)-2,5-diketopiperazine. The two hydroxyls are replaced by chlorine and the dichloro-compound made to react with sodium methylmercaptide or made into the dimercaptan, via thiourea, and this methylated. The 3,6-bis-(methylmercaptoethyl)-2,5-diketopiperazine is hydrolyzed to methionine.<sup>101, 661, 662, 663, 664</sup> Methionine has been obtained from a substituted thiazolidene.<sup>94</sup>

$\alpha$ -Amino- $\gamma$ -hydroxybutyric acid, from the lactone, is treated with potassium cyanate to form the urea,  $\text{HOCH}_2\text{CH}_2\text{CH}(\text{NHCONH}_2)\text{COOH}$ , which is converted to the hydantoin. The hydroxyl is replaced by bromine and then by MeS and the hydantoin hydrolyzed to methionine.<sup>457, 458</sup>

Homocystine,  $(\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH})_2$ , has been reduced by sodium in liquid ammonia and the mercaptide treated with methyl iodide to give methionine.<sup>756</sup> To prepare the homocystine, benzylmercaptoethyl chloride,  $\text{PhCH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ , was converted to benzyl homocysteine,  $\text{PhCH}_2\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , by the malonic ester route. The benzyl group was removed by sodium in liquid ammonia and the mercaptan oxidised to the disulfide.<sup>571a, 756, 764</sup> Starting with deuterium oxide and calcium carbide, dideuteroethylene bromide was prepared and caused to react with benzyl mercaptan to form the dideuterium bromo-sulfide,  $\text{PhCH}_2\text{SC}_2\text{H}_2\text{D}_2\text{Br}$ . The final product was dideuteromethionine.<sup>571b</sup> By using benzyl mercaptan containing radioactive sulfur,  $\text{PhCH}_2\text{S}^*\text{H}$ , the corresponding methionine,  $\text{MeS}^*\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ , has been prepared for use in tracer experiments.<sup>402, 638, 712b</sup> A microsynthesis, starting with radioactive methyl mercaptan, has been described.<sup>492.5</sup> Tagged methionine containing radioactive sulfur has been isolated from yeast grown in a medium containing radioactive sulfur.<sup>818</sup> Effecting the final methylation with radioactive methyl iodide gives the labeled methionine,  $\text{H}_3\text{C}^*\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ .<sup>509</sup> Methionine containing both labeled sulfur and labeled carbon, not in the methyl group, has been prepared.<sup>402</sup>

By similar reactions, substituting methylamine for ammonia, di-N-methylhomocystine and N-methylmethionine,  $\text{MeSCH}_2\text{CH}_2\text{CH}(\text{NHMe})\text{CO}_2\text{H}$ , have been prepared.<sup>570</sup> A Walden inver-

sion may occur in the alkylation of methionine to the N-methyl derivative.<sup>372a</sup>

Starting with benzyl-selenomercaptan,  $\text{PhCH}_2\text{SeH}$ , the selenium analog of methionine,  $\text{MeSeCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , has been made.<sup>411, 563b</sup>

A recent synthesis starts with acetoacetic ester which is treated with methylmercaptoethyl chloride and then with hydrazoic acid in the presence of sulfuric acid. This is followed by hydrolysis.<sup>214</sup>

A pilot plant for the production of racemic methionine from phthalimide, malonic ester, and methylmercaptoethyl chloride has been described in detail. The largest batch made was seventy-nine pounds.<sup>318</sup> Methods for the purification of methionine from the hydrolysis of the nitrile,  $\text{MeSCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CN}$ , have been patented.<sup>408, 442</sup>

According to a recent patent, 672 g. of acrolein is added to 324 g. hydrocyanic acid, 576 g. methyl mercaptan, 2.4 g. potassium cyanide, and 3.6 g. water in a cooled, agitated container. When the reaction is complete 228 g. of ammonia is passed in. The excess of ammonia is evaporated in vacuum. The residue is acidified with 2400 cc. of concentrated hydrochloric acid and refluxed one hour.<sup>245</sup> Impurities are removed by extraction with benzyl and other alcohols.<sup>421</sup>

To get methionine out of a mixture, it may be converted to its more soluble sulfoxide which is extracted and reduced.<sup>735b</sup>

### Resolution

When racemic methionine is incubated with the D-amino-acid oxidase of Kubs the D-isomer is oxidised to  $\alpha$ -keto- $\gamma$ -methylmercaptobutyric acid, the removal of which leaves L-methionine.<sup>213</sup> When an aqueous solution of racemic methionine and sucrose, containing baker's yeast, is kept at 25° for three days the L-isomer is destroyed and 47% of the dextro can be recovered.<sup>414</sup> Racemic methionine has been resolved by the action of papain on a mixture of carbobenzoxy-DL-methionine and aniline. The anilide of the L-isomer separates in crystal form in a yield of 95%. Acid hydrolysis gives L-methionine. The D-methionine can be recovered from the filtrate.<sup>201</sup>

When an acylated DL-methionine is exposed to the action of

certain enzymes only the acylated-L-isomer is hydrolyzed.<sup>547, 548, 587</sup> When the isopropyl ester of racemic methionine is digested with pancreatin or trypsin, the L-ester is hydrolyzed and the L-methionine recovered from the aqueous solution after the D-ester is removed by ether extraction.<sup>127, 128</sup>

Racemic methionine can be resolved by 4'-methyl-4-nitrodiphenyl-amine-2-sulfonic,<sup>775</sup>  $\alpha$ -bromo-D-camphorsulfonic,<sup>713, 788</sup> or  $\alpha$ -chloro-D-camphor- $\pi$ -sulfonic acid.<sup>714, 715.5</sup> Its acetyl derivative can be resolved with the aid of  $\alpha$ -fenchylamine.<sup>788</sup> The amide has been resolved with D-tartaric acid.<sup>712.5</sup> Methionine is racemized by acetanhydride.<sup>712.6, 762b</sup>

When radioactive racemic methionine is mixed with a large amount of one non-radioactive isomer, fractional crystallization isolates a single radioactive isomer.<sup>817</sup>

Racemic methionine and anhydrous formic acid give racemic formylmethionine, m. 100°, which can be resolved with brucine, D-isomer m. 100° [ $\alpha$ ] 25/D 10.62°, L- m. 100°, [ $\alpha$ ] 25/D -10.00°. The latter is identical with the formyl derivative of natural methionine.<sup>808b</sup> There are two forms of each of the formyl derivatives of the two active forms of methionine.<sup>669</sup>

### Physical Properties

Methionine, like other amino acids, probably exists as an inner salt and as such has no sharp melting point, at which the solid and liquid phases are in equilibrium. Melting points are reported from 270° to 283°. There does not appear to be any marked difference between the racemic synthetic and the active natural methionine.<sup>1, 48, 49a, 541b, 557, 728, 756, 808a</sup> For [ $\alpha$ ] D of L-methionine values are given ranging from -6.9° to -8.1° with one figure of -11.8°. Rotations of +8.0 to +8.8° are recorded for the D-isomer which has a negative rotation of -21.2° to -22.0° in 0.2 M hydrochloric acid and -7.5° in 0.6 M sodium bicarbonate.<sup>1, 541b, 557, 581a, 762a, 764, 808b</sup> The rotation of methionine, obtained by enzymatic hydrolysis, is the same as that from acid hydrolysis, which shows that racemization takes place very slowly, if at all, in acid solution.<sup>762a</sup> Methionine obtained by alkaline hydrolysis of protein is inactive indicating that it has been racemized by the alkali.<sup>541b</sup>

The apparent dissociation constants of methionine have been determined.<sup>229</sup> Infrared absorption<sup>449</sup> and dielectric absorption<sup>568</sup>

have been studied and curves drawn for its rotary dispersion.<sup>569</sup>

Racemic methionine has a sweet taste but is also slightly bitter.<sup>270</sup>

L-Methionine has been shown to have the same configuration as L-leucine and L-phenylalanine.<sup>387</sup>

Crystals of methionine have been described as "monoclinic plates,"<sup>557</sup> "narrow platelets,"<sup>48</sup> and "hexagonal plates."<sup>541</sup> Good crystals are difficult to obtain. They are monoclinic, hemimorphic hemihedral with axis ratios  $a:b:c$  2.09:1:3.43, with pronounced cleavage parallel to 001. The unit cell has the dimensions 9.92, 4.73, and 16.20 Å. As the density is 1.3409 there are 4 units in the cell.<sup>15</sup> DL-Methionine crystallizes in two monoclinic forms.<sup>501</sup> The crystallographic characteristics of both alpha and beta forms have been determined.<sup>200</sup>

Curves showing the relations between solubility and pH, in water and in saturated sodium chloride solution, have been published.<sup>350a</sup> The solubility of racemic methionine in 100 g. of water is 1.82 g. at 0°, 3.4 at 25° and 17.6 at 100°. <sup>198</sup> Other values are 1.818 g. at 0°, 2.995 at 20°, 3.381 at 25°, and 17.60 at 100°. The solubilities in acetic and butyric acids are also given.<sup>588</sup>

Methionine has emulsifying properties<sup>461</sup> and may be useful in photography.<sup>677a</sup>

### Reactions of Methionine

#### COMBINATIONS WITH METAL SALTS

Methionine, an alkyl sulfide, combines with mercuric chloride, and with other mercury salts. This fact has been utilized in its isolation and purification. The hydrolysate of a protein, after purification and concentration, is treated with a mercuric salt. The precipitate is decomposed by hydrogen sulfide and the methionine reprecipitated by mercuric chloride.<sup>48, 350a, 541b, 541c, 557, 581a, 581b, 581c, 707, 725a, 762a</sup> Analysis of the complex indicates a mercuric salt of methionine combined with four molecules of mercuric chloride or 2 HgCl<sub>2</sub> for each sulfide linkage.<sup>541b, 541c, 725a</sup>

The copper salt of methionine, [MeSCH<sub>2</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)-COO]<sub>2</sub>Cu, is only slightly soluble in water, 1 gram in 6 liters of hot water.<sup>541b, 541c, 557</sup> It is suitable for quantitative determination<sup>634</sup> and for microscopic identification.<sup>190</sup> Methionine and cupric chloride, in concentrated hydrochloric acid, form a deep-

orange brown compound.<sup>417a</sup> With cuprous chloride, there is a complex which has been used as a catalyst in the production of acetaldehyde from acetylene.<sup>529</sup> Methionine forms unstable silver complexes. The amino and carboxyl groups do not appear to be involved in these.<sup>562</sup>

### OXIDATION

Methionine is oxidised by enzymes.<sup>82a, 102, 814</sup> In the presence of *Aspergillus niger* 16% of it goes to the sulfate ion.<sup>285</sup> After the ingestion of methionine the urine contains increased amounts of methionine sulfoxide and  $\alpha$ -aminobutyric acid.<sup>203a</sup> In 16 hours, all of the sulfur is converted to sulfate ion.<sup>503a</sup>

In acid solution methionine is oxidised to the sulfoxide by hydrogen peroxide.<sup>723, 724, 725b, 735a</sup> Under proper conditions the oxidation is quantitative and may be the basis of an analytical method.<sup>417b</sup> It goes well in perchloric acid.<sup>417b, 722b</sup> The same oxidation can be effected by peracetic acid. The sulfoxide can be reduced back to methionine by sodium sulfite.<sup>512</sup> The preparation of the sulfoxide has been described.<sup>612, 735c</sup> Four stereoisomers are possible. These have been separated and their properties determined.<sup>439b</sup> Treating casein with hydrogen peroxide oxidises its methionine content in situ so that its hydrolysate contains no methionine.<sup>5, 78, 204, 722d</sup>

The sulfoxide inhibits glutamic acid metabolism.<sup>112b, 227, 253, 779</sup> The effects on tumors<sup>312</sup> and in diet have been studied.<sup>151, 598, 652b</sup>

Oxidation by iodine gives a cyclic compound, 1-methyl-2,1-tetrahydroazothionium-3-carboxylate.<sup>440</sup>

The sulfone,  $\text{MeSO}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , is obtained in 90% yield by the molybdate-catalyzed oxidation with hydrogen peroxide.<sup>725c</sup> This oxidation can be effected electrolytically.<sup>514, 706, 734</sup> The sulfone has none of the growth effects of methionine.<sup>73b, 77c</sup>

### SULFONIUM

Methionine combines with methyl iodide, methyl bromide, and allyl bromide to form sulfonium compounds.<sup>40, 722c, 725d</sup> When acetylmethionineallylsulfonium bromide is decomposed by alkali, methyl allyl sulfide is one of the products.<sup>725d</sup> The  $\text{MeS-}$  of methionine is thus exchanged for the bromine of allyl bromide. It is suggested that the formation and decomposition of sulfonium salts may be involved in transmethylation.<sup>722c</sup> Double sulfonium

compounds are formed with mustard gas,<sup>406, 678, 680a</sup> sesquimustard,  $(\cdot\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl})_2$ , and with nitrogen mustard.<sup>264</sup> When the one from mustard gas is heated di-(methylmercapto) ethyl sulfide,  $\text{S}(\text{CH}_2\text{CH}_2\text{SMe})_2$ , is given off.<sup>680a</sup> A methyl sulfonium derivative of methionine has been isolated from cabbage juice.<sup>489.5</sup>

### DEAMINATION

Methionine, in the presence of air, is oxidatively deaminated by an enzyme found in kidneys and livers,<sup>112a, 143, 247, 424, 777</sup> by one from snake venom,<sup>828</sup> and also by *Proteus vulgaris*:<sup>83</sup>



The corresponding hydroxyacid is produced by certain bacteria. The L-form is obtained by treatment of the amino-acid with nitrous acid.<sup>4</sup> Sodium chlorite is effective in the presence of a ketoglutarate.<sup>801</sup> Chloramine-T gives 85% deamination.<sup>184</sup> Treating methionine with potassium bromide, sodium nitrite, and sulfuric acid gives  $\gamma$ -methylmercapto- $\alpha$ -bromobutyric acid which racemizes rapidly. This with ammonia reverts to methionine. Methylamine converts it to N-methylmethionine.<sup>372a</sup>

The rate constant for the deamination of methionine and other  $\alpha$ -amino acids by nitrous acid is directly proportional to the dissociation constant of the acid and inversely proportional to the molecular weight. The rate is practically doubled by the addition of one equivalent of potassium iodide.<sup>185</sup>

### OTHER REACTIONS

Methionine forms a picrolonate.<sup>212, 808a</sup> Its choline salt is said to be valuable in the treatment of diseases of the liver.<sup>413a, 413c</sup> The solubility of its salt with 5-nitrobarbaturic acid has been determined.<sup>596</sup> Compounds with penicillin derivatives have been prepared.<sup>351.5</sup>

The chloroacetyl derivative of methionine and ammonia give glycyl-L-methionine, m. 140–5°.<sup>347a</sup> A peptide may be prepared by treating the phenyl ester of methionine with a tertiary base and an aminoacid.<sup>800.5</sup> A number of such peptides have been made.<sup>129, 178, 202, 702</sup>

The amino group can be methylated.<sup>372a</sup> It reacts normally with acid chlorides such as *p*-nitrobenzoyl chloride<sup>404, 824</sup> and allyl chloroformate,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{OCOCl}$ .<sup>692</sup> The N-nicotinyl

derivative of the ester is formed from nicotiny azide.<sup>371</sup> The sulfide,  $\text{MeSCH}_2\text{CH}_2\text{CH}(\text{NHCH}_2\text{CH}_2\text{SCH}_2\text{Ph})\text{CO}_2\text{H}$ , has been prepared with the aid of  $\beta$ -chloroethyl benzyl sulfide,  $\text{PhCH}_2\text{-SCH}_2\text{CH}_2\text{Cl}$ .<sup>766</sup>

Methionine may add to one or to two molecules of acrylonitrile to change the amino group into  $\text{-NHCH}_2\text{CH}_2\text{CN}$  or into  $\text{-N}(\text{CH}_2\text{CH}_2\text{CN})_2$ .<sup>488</sup>

Methionine suspended in absolute alcohol, treated with hydrogen chloride until it dissolves, gives the ethyl ester.<sup>110, 355, 509.5</sup> Crude methionine can be purified by conversion to the ester which may be fractionated.<sup>707</sup> The hydrochloride of the ester, m.  $56^\circ$ , is soluble in water.<sup>355</sup> The isopropyl ester has been described.<sup>128</sup> The thiobenzoyl derivative,  $\text{PhCSNHCH}(\text{CH}_2\text{CH}_2\text{SMe})\text{CO}_2\text{Et}$ , has been prepared.<sup>408.5</sup> Phenylmagnesium bromide reacts with the ester to give the tertiary alcohol, 1,1-diphenyl-4-methylmercapto-2-aminobutanol-1.<sup>387</sup>

Methionine is desulfurized by active Raney nickel to L- $\alpha$ -amino-butyric acid. This is further evidence of the configuration of natural methionine.<sup>249, 539, 774</sup> Electrolytic reduction eliminates the sulfur as hydrogen sulfide and methyl mercaptan.<sup>514, 706</sup> Methionine is decomposed by *Clostridium tetanomorphum*.<sup>820</sup> Sodium in liquid ammonia converts it to homocysteine,  $\text{HSCH}_2\text{-CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ .<sup>683c</sup> Heating it with 60% sulfuric acid, to  $130^\circ$  for 8 hours, accomplishes the same result.<sup>142</sup>

Methionine heated in liquid paraffin to  $250^\circ$  is decarboxylated to 3-methylmercaptopropylamine,  $\text{MeSCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ .<sup>739b</sup> In the presence of alkali, methionine and methylisothiurea,  $\text{MeSC}(\text{:NH})\text{NH}_2$ , give guanidomethionine.<sup>370, 538</sup> Methionine, autoclaved with formaldehyde at  $110^\circ$ , forms a compound that has a blue-violet fluorescence.<sup>462</sup> 2-Hydroxy- $\alpha$ -naphthoic aldehyde and methionine condense to a Schiff's base.<sup>485</sup> Methionine takes up one-third of its weight of nitrogen trichloride. The product causes paralysis in a dog's legs.<sup>79</sup> Treating methionine sulfoxide with hydrazoic acid gives a factor similar to that formed from protein with nitrogen trichloride.<sup>80, 526</sup>

### Detection and Estimation

Methionine can be detected by fusion with sodium hydroxide containing some water. The melt is acidified and the methyl mercaptan passed into lead acetate solution or into a solution of

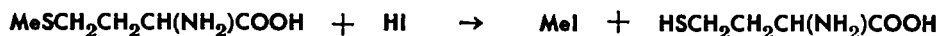
0.2 g. isatin in 100 cc. concentrated sulfuric acid. The yellow solution turns grass green. This test is sensitive to 0.2 mg. methionine.<sup>739a</sup> Colors are developed when ammonium thiocyanate is heated with amino-acids, red for methionine and several others.<sup>369</sup> Dry methionine gives a yellow color with a solution of anhydrous copper sulfate in concentrated sulfuric acid.<sup>667</sup> A strip of photographic film bathed in 0.1% methionine solution, dried in warm air from an electric fan and developed, shows black spots due to copper particles from the fan brushes.<sup>677b</sup> Amino-acids are identified by the derivatives obtained by treatment with *p*-toluene sulfonyl chloride.<sup>477</sup> Methionine and the chloride of azobenzenecarboxylic acid,  $\text{PhN:NC}_6\text{H}_4\text{COCl}$ , give a compound, m.  $119^\circ$ ,  $[\alpha]$   $12/608 -27.32^\circ$ .<sup>390</sup> Optical and crystallographic properties are given for the diluturic<sup>487</sup> and 2-nitro-1,3-indandione<sup>438</sup> derivatives of methionine. *p*-Iodotoluene-sulfonyl chloride containing I 131 has been used for making methionine derivatives of which minute amounts can be traced.<sup>744</sup>

For the micro identification of methionine its solution is mixed with a solution of copper acetate or of platinic chloride and sodium iodide.<sup>21</sup> It may be determined by oxidising it completely and precipitating the sulfuric acid with benzidine. The precipitate is titrated with alkali.<sup>202</sup>

Methionine sulfoxide gives the ninhydrin reaction.<sup>586</sup>

The analysis of the complex mixture of amino-acids present in protein hydrolysates is not a simple matter. The methods have been discussed.<sup>221</sup> A countercurrent extraction plan using chloroform and water, has been devised for the separation of such mixtures.<sup>497</sup> Recently chromatographic methods have been devised.<sup>182, 197, 304b, 315, 427, 535, 567, 585, 611, 633, 655, 680b, 718, 721, 725e, 738, 809, 827</sup> Differences in the mobilities of the ions may be utilized by ionophoresis in a slab of silica jelly.<sup>176a</sup> Advantage may be taken of the differences in acid strengths of the amino-acids for separations by ion exchange resins.

The most distinctive thing about methionine is the presence of the  $\text{MeS-}$  group. The Baernstein method is the sulfur version of the Zeisel methoxyl determination. Methyl iodide is evolved when methionine is boiled with concentrated hydriodic acid and the liberated methyl iodide is caught in silver nitrate solution:





The  $\gamma$ -mercapto- $\alpha$ -aminobutyric acid condenses to the thiolactone.<sup>43</sup> This method has been widely used and modified from time to time.<sup>34, 63, 125, 282a, 392, 393b, 445a, 465b, 708, 765, 770</sup> Some methyl mercaptan and hydrogen sulfide may be formed also.<sup>392</sup> The thiolactone may be determined as a check.<sup>63</sup>

The method of McCarthy and Sullivan depends on the color which develops when methionine is treated with sodium nitroprusside. The yellow color turns to red on acidification. The estimation is colorimetric and must be done promptly as the color soon fades.<sup>104a, 164, 188, 360a, 476, 495, 620, 799</sup>

The sulfur in methionine can be determined by the Benedict-Denis method,<sup>76</sup> the chief feature of which is fusion with cupric nitrate.<sup>564, 622, 778</sup> Methionine is oxidised selectively and quantitatively by hydrogen peroxide in perchloric acid solution. This is a basis of a volumetric method.<sup>6, 417b</sup> On the other hand cystine and cysteine are oxidised to sulfate ion by nitric acid while methionine is not. If the total sulfur is known the methionine is found by difference.<sup>232a</sup> Another plan is to estimate the cystine by reduction and treatment with cuprous oxide, subtracting this from the total sulfur.<sup>63, 430</sup> Methionine may be burned in the Parr bomb.<sup>144, 564</sup>

Methionine forms a periodide, while other sulfur compounds do not. This is the basis of an iodometric determination.<sup>45, 439a, 584</sup>

The bioassay of methionine can be accomplished by the use of various organisms. The methods have been reviewed.<sup>52a</sup> A number of references are given without comment.<sup>53, 57, 115, 210, 211, 287b, 291, 354, 360b, 471, 472, 602b, 647, 657, 698</sup>

### Methionine an Essential

From a mass of experimentation the conclusion has been reached that methionine is essential to the growth and well being of animals. The same holds for bacteria. Methionine is now listed as one of the ten essential amino acids. A few references are given.<sup>8, 9, 12, 18b, 39, 75, 103, 109, 131, 140, 207, 211, 232b, 257, 357, 363, 399, 400, 409, 420, 428, 433, 434, 435, 444, 480, 489, 551, 614b, 614c, 615, 616, 617, 675, 740, 780, 783, 792, 800, 815, 816</sup>

To a certain extent a mixture of choline and homocystine may function as methionine.<sup>158, 752b, 753</sup> The deamination product of methionine,  $\alpha$ -keto- $\gamma$ -methylmercaptobutyric acid,  $\text{MeSCH}_2\text{CH}_2\text{-COCOOH}$ , may replace methionine under certain conditions.<sup>143</sup> The same is true of the corresponding  $\alpha$ -hydroxy-acid.<sup>105</sup>

### Efficiency of Racemic and of Dextro

As is well known, in many biological processes either the one or the other of the two optically active isomers is utilized while the other is not. Since the synthesis of racemic methionine and its resolution the question of the efficacy of the dextro isomer has been extensively investigated. The D-isomer is more efficient in methylating ethanolamine or dimethylethanolamine,  $\text{Me}_2\text{NCH}_2\text{-CH}_2\text{OH}$ , than the L-form.<sup>676b</sup> From feeding experiments the general conclusion is that the unnatural isomer is utilized by organisms but not quite so well as the natural. Hence the racemic is much better than half its weight of the natural but not quite so good as twice that amount. A number of references are given without any attempt at analysis.<sup>7, 29, 55b, 77a, 85, 87, 193, 199, 206, 217, 276b, 287a, 316, 321, 322, 373a, 373b, 378, 451, 452, 459, 515, 518, 524, 541d, 618, 627, 671, 682a, 697a, 716, 757, 802</sup>

### Origin and Fate of Methionine

How does methionine come to be and what happens to it when it ceases to be methionine? In spite of much painstaking investigation only partial answers can be given to these questions. Methionine is only one of the amino-acids from which proteins are built. Its chemistry is so intertwined with that of all the others that we will probably not understand it fully until we know the whole story of proteins.

To state that methionine is one of the amino-acids which are essential to the growth and well-being of animals is another way of saying that animals can not manufacture it, or enough of it, to meet their requirements. The methionine content of vegetable proteins is strikingly like that of the animal yet plants of the most diverse sorts must be able to synthesize it from simple materials. The only sulfur available to plants is that of sulfates such as gypsum.

Various theories of the biosynthesis of methionine have been advanced.<sup>209, 263, 552c, 603</sup>

A deal of careful experimenting has been done on the transformations of methionine into other compounds. By feeding experiments, a number of facts have been established and various plausible hypotheses built up. The subject has been reviewed by several.<sup>335, 453a, 532, 755</sup> A few experimental papers are listed.

Too much space would be required to go into the findings.<sup>4, 23, 24, 54, 83, 93, 117, 118a, 120, 216b, 269, 329, 394, 426, 445b, 503a, 581b, 618, 682a, 685, 719b, 742, 771, 773, 777</sup>

A number of experiments have been made with methionine labeled with radioactive sulfur, administered in different ways. The distribution of the radioactive sulfur in the various organs was traced readily, but to determine the compounds into which it went was not so easy.<sup>259, 260, 261, 425, 473, 507, 637, 709, 710, 711, 712a, 712b, 790</sup> Radioactive cystine was found in two cases<sup>507, 712a, 712b</sup> and taurine in one.<sup>712a, 712b</sup>

In one experiment L-methionine, the methyl group of which contained radioactive carbon, was fed to a rat. In 52 hours 32.4% of the radioactive carbon appeared as respiratory carbon dioxide and 14.6% was found in the urine.<sup>487</sup> In another, the methyl group contained deuterium and radioactive carbon. This was fed to a rat on choline-free diet. Choline was isolated and found to contain deuterium and radioactive carbon in the original ratio showing the methyl group had been transferred as a whole.<sup>396</sup> Analysis of the cystine from rats fed on methionine containing isotopes of sulfur and carbon showed that 80% of its sulfur but no significant amount of its carbon had been derived from the tagged methionine.<sup>760</sup>

A tagged methyl group from methionine was used in converting guanidoacetic acid to creatine.<sup>751, 754</sup>

### Transmethylation

There is abundant evidence that, in the processes involved in growth in animals, methyl groups are transferred. They appear to be taken from one compound to build up another. Methionine, choline, betaine, creatine, homocysteine, guanidoacetic acid, and probably others take part in this game of passing around methyl groups. Just how the transfer is effected is difficult to understand. In methionine the methyl group is joined to sulfur. Experience with sulfides and mercaptans shows that this is a strong bond. In the oxidation of methionine the methyl remains attached to the sulfur. Boiling with concentrated hydriodic acid does break off the methyl group as methyl iodide but that is drastic treatment. It is well known that many reactions, which, in the laboratory, can be made to take place only by the aid of high temperatures, high pressures, strong acids or alkalies, or powerful

catalysts, go on *in vivo* under the mildest conditions. This subject has been reviewed.<sup>17a, 42, 135, 298b, 746a, 752a</sup>

There have been many feeding experiments in which transmethylation appears to have been demonstrated.<sup>50, 66, 113, 228, 289, 384, 504, 576, 676a, 676b, 741</sup> Methionine sulfoxide also serves as a methyl group donor.<sup>676a, 676b, 741</sup> This has been supposed to be due to the fact that the sulfoxide can be reduced to methionine,<sup>316</sup> but might possibly be due to the decomposition of the sulfoxide into formaldehyde and homocysteine. The sulfone, which can not be reduced, is biologically inactive.<sup>316</sup>

When certain bacteria are grown in a medium containing methionine and glucose, methyl mercaptan and methyl sulfide are produced.<sup>156</sup> Methionine gives methyl sulfide but no mercaptan in bread cultures of *S. brevicaulis*.<sup>157</sup> The most definite experiments are those in which methionine containing a deuteromethyl group has been fed to animals, and deuteriocholine, deuterocreatine, and deuterio-creatinine found later. The deuteromethyl group passed to choline from methionine.<sup>175, 396, 649, 650, 651, 751, 754</sup> The whole scheme of transmethylation has been worked out with radioactive carbon.<sup>746b</sup>

### Methionine in Nutrition

The literature on methionine in nutrition, particularly as relates to growth, is so extensive that it is impossible to go into any detail as to the findings. It may be mentioned that it influences the metabolism of nitrogen,<sup>16, 82b, 138, 161, 450, 460, 521, 606</sup> that it is absorbed rapidly by the intestine,<sup>26, 133, 162, 196, 240, 373b, 822, 823</sup> and that an excess of methionine may retard growth.<sup>132, 806</sup> Other references are given without any attempt at classification.<sup>10, 11, 17a, 17b, 18a, 18b, 19, 20, 22, 31, 55a, 64, 77a, 77b, 81, 84, 88, 89, 97, 98, 99, 108, 111, 136, 138, 154, 163, 165, 166, 167, 174, 183, 186, 194, 195, 199, 233a, 233b, 242, 243, 269, 275, 276a, 278, 284, 287a, 287b, 297, 298a, 299a, 301a, 302, 308, 309, 310, 313, 314, 328, 331, 332, 334, 337, 345b, 348, 373b, 377, 378, 383, 384, 385, 386, 397, 398, 401, 409, 410b, 415, 418, 422, 423, 441, 443, 448, 463, 464, 469, 478, 481, 482, 483, 484, 489, 490, 493, 496, 499, 502, 508, 515, 518, 519, 520, 525, 527, 528, 540, 542, 544, 545, 550, 554, 556, 559, 561, 566, 572, 573, 574, 578, 594, 595, 601, 604, 605, 606, 609, 610, 614c, 614d, 614e, 615, 619, 621, 624, 627, 629, 641, 642, 648, 658, 670, 672, 680a, 689, 693, 695, 703, 704, 716, 717, 719a, 729, 736b, 743, 752b, 753, 759, 772, 781, 782, 787, 791a, 791b, 793, 821</sup>

### Methionine as a Protective Agent

Methionine protects the liver against injury under various circumstances.<sup>228, 277, 283, 351, 474</sup> It is beneficial in burns,<sup>186, 187, 333, 475</sup> and in other physiological disturbances.<sup>124, 301a, 301b, 491, 673, 683a</sup> It has some antibacterial action<sup>69, 290</sup> and is synergistic with penicillin<sup>636</sup> but favors the fermentation of glucose by propionic acid bacteria.<sup>153</sup> According to one investigator injection or ingestion of methionine delays coagulation of the blood<sup>688</sup> but another finds that it has no such effect.<sup>807</sup> Deficiency of methionine did not affect the healing of wounds.<sup>705</sup> The racemic acid did not influence the growth of tumor cells.<sup>468</sup> It reversed the antibacterial action of methoxinine.<sup>608</sup>

Methionine counteracts the effects of serine,<sup>776</sup> methylcholanthrene,<sup>798</sup>  $\beta$ -alanine, and pantothenic acid<sup>555</sup> and inhibits the combination of iodine with casein.<sup>145</sup>

Methionine is antagonistic to the sulfa drugs,<sup>323, 599, 645, 700, 810</sup> sulfanilamide,<sup>416, 645, 700, 810</sup> sulfathiazole,<sup>810</sup> sulfadiazine,<sup>38, 733</sup> to *p*-dimethylaminobenzene,<sup>796</sup> nicotinamide,<sup>317, 591</sup> and thyroxine.<sup>2b</sup> It counteracts the damage done by chloroform,<sup>280, 522, 523</sup> carbon tetrachloride,<sup>37, 67, 73a, 74, 208, 219, 268, 307, 639</sup> ethylene chloride,<sup>338, 340, 341, 343</sup> propylene chloride,<sup>338, 339</sup> benzyl chloride,<sup>683b</sup> bromobenzene,<sup>683b, 794</sup> *p*-bromobenzyl bromide,<sup>683b</sup> iodoacetic acid,<sup>694, 791b, 795</sup> naphthalene, phenanthrene,<sup>683b</sup> trinitrotoluene,<sup>219, 659</sup> biphenyl, chrysene,<sup>785</sup> dimethylaminoazobenzene,<sup>305, 797</sup> phenylmercury borate,<sup>565</sup> certain gold,<sup>498</sup> nickel, and cobalt<sup>300</sup> compounds, selenic acid,<sup>238</sup> quinoline,<sup>181b</sup> piperidine,<sup>181b</sup> pyridine,<sup>58, 59, 181b</sup> coumarin,<sup>592</sup> norleucine,<sup>319</sup> and  $\beta$ -furyl-DL-alanine.<sup>168</sup>

It appears that in the detoxification of some, at least, of these agents, aminoacid sulfur is used up.<sup>683b</sup> The result may be a depletion of methionine and cystine to such an extent that normal metabolism can not go on. The administration of methionine may remedy this condition.<sup>231</sup>

Methionine has a preservative action on liquid eggs before drying.<sup>330</sup> It has a synergistic effect with phenolic antioxidants.<sup>171</sup>

### Methionine and the Liver

There have been many studies on methionine and the liver, particularly as relates to the deposition of fats in that organ.

Some references are given without going into details as to their findings.<sup>2a, 35, 36, 46, 47, 65, 68, 70, 85, 92, 152, 159, 160, 169, 181a, 203c, 218, 219, 235, 236, 256, 288, 298a, 299b, 304a, 306, 327, 342, 345a, 349, 358, 362, 365, 405, 436, 500, 505, 537, 575, 602a, 613, 652a, 690, 691, 730, 731, 736a, 737, 789, 805, 825</sup>

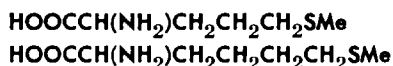
### Cystinuria

There have been special studies of the metabolism of methionine in cystinuria.<sup>25, 27, 116, 118b, 119, 121, 122, 172, 347b, 454</sup> When radioactive methionine was injected into normal or cystinuric dogs 97% of it was retained.<sup>712c</sup>

### Methionine Type Compounds

#### HOMOLOGS

Two homologs have been prepared:



The sodium derivative of phthalimidomalonate ester was caused to react with an excess of trimethylene, or tetramethylene, bromide and the resulting bromide converted to the mercaptan which was methylated. The first melts at 272–4° and the second at 276–8° with decomposition.<sup>216a, 379, 758</sup>

The S-benzyl derivatives of these,  $\text{PhCH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$  and  $\text{PhCH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , were prepared by the same authors along with the methyl derivatives. The first of these and its  $\delta$ -methyl derivative,  $\text{PhCH}_2\text{SCHMeCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , have been prepared by another group.<sup>150</sup>

#### ETHIONINE



Ethionine, which is not found in natural products, has been synthesized by methods analogous to those that have been used for methionine.<sup>150, 215, 431b, 582, 784</sup> It melts, or rather decomposes, at 265–84°.<sup>215, 431b</sup> It can not replace methionine in feeding,<sup>112b, 215, 320, 686b, 779</sup> though it does prevent the accumulation of liver fat.<sup>320</sup> Ethionine, the ethyl group of which was tagged, was fed to a rat. The radioactivity was found in the creatin and choline

of the tissues.<sup>687</sup> The corresponding S-butyl compound has been prepared.<sup>81.5</sup>

### BENZYL HOMOCYSTEINE

This has been mentioned as an intermediate in one synthesis of methionine which started with benzylmercaptoethyl chloride.<sup>714.5</sup> It can be prepared in the usual way from homocysteine and benzyl chloride.<sup>142</sup> It can be debenzylated by sodium in liquid ammonia.<sup>600</sup> The optically active isomers of its acetyl derivatives have been separated enzymatically.<sup>597</sup> It is converted *in vivo* by rats to the acetyl derivative.<sup>768</sup> Labeled S<sup>35</sup> it has been used in feeding experiments.<sup>589</sup>

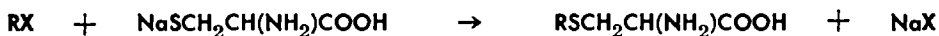
### CARBOXYALKYL DERIVATIVES

The two acids, HO<sub>2</sub>CCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)COOH, and HO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>CH(NH<sub>2</sub>)COOH, are made by adding the corresponding halide acids to methionine which has been demethylated by sodium in liquid ammonia.<sup>683c</sup>

### ALKYL CYSTEINYL DERIVATIVES

#### RSCH<sub>2</sub>CH(NH<sub>2</sub>)COOH

These have been made in considerable number and variety. Cysteine, its esters, and its acylamino derivatives react regularly with simple, or complex, alkyl halides in alkaline solution:



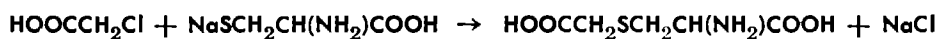
The methyl,<sup>372b, 761</sup> ethyl,<sup>130, 170, 179, 180, 699</sup> propyl,<sup>699</sup> *i*-propyl,<sup>274, 699</sup> butyl,<sup>372b, 699</sup> allyl,<sup>699</sup> and benzyl<sup>170, 336, 372b, 682c, 699, 747</sup> derivatives been prepared in this way. From more complex halides corresponding derivatives have been prepared, such as PhSCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH(NH<sub>2</sub>)CO<sub>2</sub>H,<sup>251</sup> HOCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH(NH<sub>2</sub>)COOH,<sup>286</sup> S[CH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH(NH<sub>2</sub>)COOH]<sub>2</sub>,<sup>674, 681</sup> and HOCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH(NH<sub>2</sub>)COOH.<sup>279</sup> The ethylene and trimethylene derivatives have been reported.<sup>642.5</sup> The benzyl derivative of DL-cysteine has been made from sodium benzyl mercaptide and diethyl α-acetamido-α-dimethylaminomethylmalonate methiodide.<sup>40.5</sup> The methyl and benzyl derivatives have been obtained by the hydrolysis of the corresponding hydantoins.<sup>546</sup> The benzyl derivative is formed when silk, or

dried milk, is heated with alkali and treated with benzyl mercaptan.<sup>553</sup>

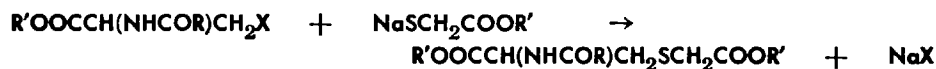
Compounds of this class have been obtained by starting with the addition products of mercaptans to certain unsaturates.<sup>149, 177, 180, 225, 303, 701, 715</sup> The sulfoxides,  $\text{PhSOCH}_2\text{CH}_2\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$  and  $\text{OS}[\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}]_2$ , have been made by adding cysteine to phenyl vinyl sulfoxide,  $\text{PhSOCH}:\text{CH}_2$ , and to divinyl sulfoxide,  $\text{OS}(\text{CH}:\text{CH}_2)_2$ , respectively.<sup>251, 252, 577</sup>

The addition of thiophenol to  $\alpha$ -aminoacrylic acid, under the catalytic influence of piperidine, gives the acid,  $\text{PhSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ ,<sup>72</sup> which is also formed from diphenyliodonium chloride and cysteine.<sup>625</sup> The N-acetyl derivative of this acid has been obtained from benzenediazonium chloride and N-acetylcysteine.<sup>56, 826</sup> A small amount of this is secreted by a rat to which benzene has been fed.<sup>826</sup> The corresponding naphthalene acid,  $\alpha\text{-C}_{10}\text{H}_7\text{SCH}_2\text{CH}(\text{NHAc})\text{COOH}$ , has been made similarly.<sup>367</sup> It is secreted after the ingestion of naphthalene.<sup>114</sup> *S-p*-Chlorophenylcysteine,  $p\text{-ClC}_6\text{H}_4\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ ,<sup>786</sup> and the corresponding fluorine acid,  $p\text{-FC}_6\text{H}_4\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ ,<sup>826</sup> have been made through the diazo reaction.

The ester,  $p\text{-MeC}_6\text{H}_4\text{SCHPhCH}(\text{NHCOPh})\text{CONHCH}_2\text{COOEt}$ , has been made by the addition of *p*-thiocresol to  $\text{PhCH}:\text{C}(\text{NHCOPh})\text{CONHCH}_2\text{COOEt}$ .<sup>552b</sup> The reaction of *p*-thiocresol with 2-phenyl-4-benzal-5-oxazolone gives  $p\text{-MeC}_6\text{H}_4\text{SCHPhCH}(\text{NHCOPh})\text{COOEt}$ .<sup>552a</sup> Other compounds containing substituents in the  $\beta$ -position have been taken up under penicillamine, chapter 5, Volume I. Thioglycolic acid and the azlactone of  $\alpha$ -benzamidoacetic acid give ethyl  $\alpha$ -benzamido- $\beta$ -(carbethoxymethylmercapto)butyrate.<sup>134, 622.5</sup> Thioglycolic acid and ethyl 2-benzamido-7-carbethoxy-2-heptenoate give ethyl  $\alpha$ -benzamido- $\beta$ -(carbethoxymethylmercapto)suberate.<sup>83.5, 622.5</sup> This is a step in one biotin synthesis, see chapter 1. Dibasic acids are obtained readily by the reaction of a halogen acid with cysteine in alkaline solution.<sup>325, 389, 593</sup>



Naturally the same product is obtained when the positions of the halogen and mercaptan group are reversed: <sup>324b, 326</sup>





A number of acids and their esters of this type have been made <sup>141, 324a, 324b, 391, 510a, 533, 534, 580, 813</sup> in connection with the synthesis of biotin. A tribasic aminosulfide acid is produced by the addition of cysteine to maleic acid in the presence of piperidine.<sup>536</sup>

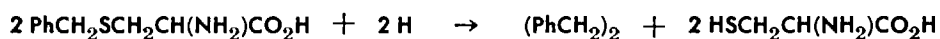
The same end may be attained by starting with a sulfide and introducing the amino and carboxyl groups. Thus benzylmercaptoacetaldehyde,  $\text{PhCH}_2\text{SCH}_2\text{CHO}$ , is converted to the cyanhydrin,  $\text{PhCH}_2\text{SCH}_2\text{CH}(\text{OH})\text{CN}$ , which is treated with ammonia and then hydrolyzed to  $\text{PhCH}_2\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ .<sup>273</sup>

Djenkolic acid,  $\text{H}_2\text{C}[\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}]_2$ , which might be called methylene dicysteine, is a thioformal and is taken up in chapter 5, Volume I.

The cysteine hemimercaptals,  $\text{HOCH}_2\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ ,  $\text{PrCH}(\text{OH})\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , hemimercaptole,  $\text{MeC}(\text{OH})-(\text{COOH})\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ ,<sup>635</sup> and mercaptals with acetaldehyde, propionaldehyde, and benzaldehyde<sup>33</sup> are S-alkyl derivatives.

The amino group of an S-alkylcysteine can be benzoylated<sup>324a, 533, 534, 699</sup> or acetylated<sup>699, 813</sup> by standard methods. The S-benzyl is racemized by an excess of acetanhydride. This gives a route to D-cysteine.<sup>819</sup> The S-benzyl<sup>682b</sup> and other<sup>767</sup> cysteine derivatives are acetylated *in vivo* when fed to animals.

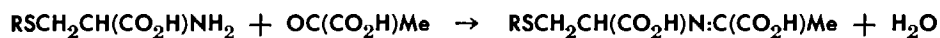
S-Benzylcysteine is reduced readily by sodium in liquid ammonia:<sup>646</sup>



This has been used frequently in syntheses.

The sulfide bond in compounds of this class may be split by silver salts under mild conditions.<sup>577</sup>

An alkylcysteine reacts with pyruvic acid to form a Schiff's base:<sup>344</sup>



The melting points and rotations of a number of S-alkylcysteines have been given.<sup>32</sup> As all of them are inner salts the "melting points" are high, from 222–256°, and are to be considered as decomposition temperatures. They can be relied upon for characterization only when the heating is done under care-

fully controlled conditions. A direct comparison of the unknown with an authentic sample of the known is desirable.

The S-methyl,<sup>80</sup> S-ethyl, S-propyl, S-*i*-propyl, S-butyl, and S-benzyl derivatives of cysteine are oxidised by hydrogen peroxide to their sulfoxides. Alliin, which is said to be the "mother substance" of garlic oil, is S-allylcysteine sulfoxide,  $\text{CH}_2:\text{CHCH}_2\text{-SOCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ .<sup>699</sup> S-Methylcysteine is oxidised when fed to a dog but the ethyl and benzyl are not.<sup>581b</sup> The S-ethyl derivative is oxidised slowly on slices of rat liver.<sup>581d</sup>

The infrared spectra of a number of aromatic mercapturic acids,  $\text{ArSCH}_2\text{CH}(\text{CO}_2\text{H})\text{NHCOMe}$  have been recorded.<sup>266, 382</sup>

Two selenium compounds have been prepared,  $\text{PhSeCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ <sup>486, 563a</sup> and  $\text{PhCH}_2\text{SeCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ .<sup>563a, 804</sup>

### LANTHIONINE

This recently discovered sulfide-amino-acid is closely related to cystine, the well-known disulfide acid.



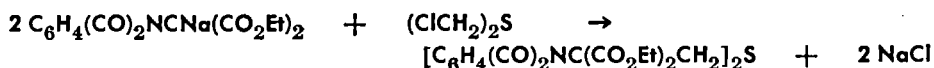
Lanthionine was first isolated by the acid hydrolysis of wool, which had been boiled one hour with 2% sodium carbonate solution.<sup>361, 369.5</sup> Heating wool with a mildly alkaline buffer is sufficient.<sup>173</sup> It has been obtained from horses' hoofs,<sup>644</sup> keratin, and other proteins,<sup>359b, 361</sup> also from insulin.<sup>749</sup> An alkali cyanide is suitable for the hydrolysis since it is alkaline and takes up sulfur.<sup>237</sup> Lanthionine accounts for 10% of the sulfur in subtilin hydrolyzates.<sup>157</sup>

Lanthionine has been synthesized from cysteine and  $\beta$ -chloro- $\alpha$ -aminopropionic ester:<sup>135b, 748</sup>

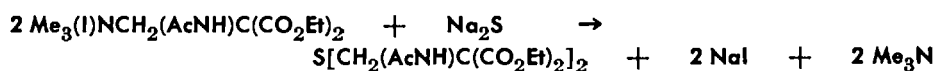


For simplicity the free acids are written instead of the salts and ester. Closely related to this is the preparation of the dimethyl ester of dibenzoyllanthionine from methyl  $\alpha$ -benzamido- $\beta$ -chloropropionate and sodium sulfide.<sup>265</sup> Another synthesis is from the

sodium derivative of phthalimidomalonic ester and  $\alpha, \alpha'$ -dichloromethyl sulfide:



Hydrolysis of this gave the lanthionine.<sup>431a</sup> In a recent synthesis diethyl  $\alpha$ -acetamido- $\alpha$ -dimethylaminomethylmalonate methiodide is heated with sodium sulfide:



The product is saponified, deacetylated, and decarboxylated.

There are four forms of lanthionine, meso, racemic, and the two optically active. The racemic is 7 times as soluble in water as the meso.<sup>361</sup> The racemic and the active forms decompose at the same temperature, 293–5°. The dibenzoyl derivatives of the active melt at 202–4° and have rotations +8° and –8°. This derivative of the meso melts at 184°. <sup>135b</sup> The racemic form has been found in the mother liquor from the meso prepared from egg shells.<sup>368</sup>

The isolation of lanthionine is chiefly a matter of separating it from cystine. Advantage is taken of the fact that the sodium salt of the N,N'-dibenzoyl derivative of cystine,  $(\text{SCH}_2\text{CH}(\text{NHCOPh})\text{COOH})_2$ , is practically insoluble in water.<sup>623, 630a</sup>

There is little, if any lanthionine present in proteins. That which is gotten out appears to have been derived from cystine. It is well known that treatment of wool, hair, and the like, with alkali takes out a considerable amount of sulfur.<sup>631</sup> The transformation of cystine to lanthionine is largely responsible for this.<sup>630a</sup> In one instance cow's hair treated with alkali and then hydrolyzed yielded 2% of lanthionine but none if hydrolyzed directly.<sup>623</sup>

The change of cystine to lanthionine by the loss of an atom of sulfur is easy to write:



To explain how this takes place is a different matter. It is the cystine of the intact protein chain that loses the sulfur, since the structure of wool fiber is not greatly changed by this loss.<sup>630c</sup> Several mechanisms have been suggested. In one cystine is sup-

posed to be converted to cysteine a part of which loses hydrogen sulfide to form  $\alpha$ -aminoacrylic acid:



The other part of the cysteine adds to this:<sup>553, 630c</sup>



In another, cystine is supposed to break into  $\alpha$ -aminoacrylic acid and  $\text{HSSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ , which passes into cysteine by loss of sulfur. Addition then takes place.<sup>530</sup> In support of this it has been shown that the addition of cysteine to acrylic acid can be effected readily in neutral or slightly alkaline solution. The product,  $\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{SCH}_2\text{CH}_2\text{COOH}$ , lacks one amino group of being lanthionine.<sup>632a</sup> The fact that such a large proportion of the cystine present is accounted for by the lanthionine produced makes the explanation more difficult. It has been stated that half of the cystine of wool goes into lanthionine, by alkali treatment, and the other half into combined  $\alpha$ -aminoacrylic acid.<sup>148, 192</sup> Treatment with formic acid at 70–100° aids the conversion.<sup>513</sup>

Lanthionine can be identified in hydrolyzates by paper chromatography.<sup>176b</sup> It gives a red color when heated with potassium thiocyanate.<sup>369</sup> It can be determined, with an accuracy of 97–8%, by conversion to cysteine by hydriodic acid.<sup>347c</sup>

Lanthionine supported a fair growth of *Proteus Morganii*<sup>511</sup> but failed with rats.<sup>380, 381</sup>

A monomethyl-lanthionine,  $\text{HO}_2\text{CCH}(\text{NH}_2)\text{CHMeSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ , has been isolated from the hydrolyzate of the anti-biotic peptide, subtilin.<sup>15.5</sup> A dimethyl-lanthionine,  $\text{HO}_2\text{CCH}(\text{NH}_2)\text{CMe}_2\text{SCH}_2\text{CH}(\text{NHCOR})\text{CO}_2\text{H}$ , has been made by adding  $\beta,\beta$ -dimethylcysteine to an  $\alpha$ -acylaminoacrylic acid.<sup>386.5</sup>

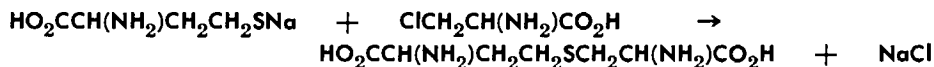
#### CYSTATHIONINE



This is an unsymmetrical sulfide, one end from cysteine and the other from homocysteine. The name relates it to cystine and methionine. A crystalline compound containing two carboxyl and two amino groups and one sulfur atom was isolated from the products obtained by treating wool with sodium sulfide.<sup>118a, 135a, 429</sup> It has been obtained from horses' hoofs.<sup>643</sup> There was isolated

from a vetch growing in a seleniferous region an amino acid of the composition,  $C_{21}H_{44}N_6Se_2SO_{12}$ , which was considered to be an isomorphous mixture of cystathionine with its selenium analog.<sup>359a</sup>

The first synthesis was from homocysteine and  $\beta$ -chloro- $\alpha$ -aminopropionic acid:



The homocysteine was dissolved in liquid ammonia, containing sodium, and the chloro compound added.<sup>135a, 750</sup> Several optical isomers were obtained by starting with different forms of the two reactants.<sup>28</sup> In another synthesis the cystine is reduced by sodium in liquid ammonia and 3,6-bis(2-chloroethyl)-2,5-diketopiperazine added. The reaction product is hydrolyzed by dilute hydrochloric acid.<sup>30, 682d, 684, 784</sup> In still another, homocysteine-thiolactone is heated with  $\alpha$ -aminoacrylic acid. The mercaptan corresponding to the thiolactone adds across the double bond.<sup>632b</sup> L-Cystathionine containing radioactive sulfur has been synthesized for use in feeding experiments.<sup>589</sup>

The chromatographic separation of cystathionine from methionine and other related substances has been studied.<sup>655</sup>

Cystathionine is cleaved by a rat liver enzyme to cysteine. It may be an intermediate in the transformation of methionine to cysteine.<sup>95, 96</sup> The diketopiperazine of cystathionine does not support growth in rats.<sup>686c</sup>

#### HOMOLANTHIONINE



This is related to homocysteine in the same way that lanthionine is to cysteine. It can be obtained by the acid hydrolysis of 3,6-bis-[2-(3-amino-3-carboxypropylmercaptoethyl)]-2,5-diketopiperazine.<sup>682d, 784</sup> Chromatographic methods are useful for the separation of homolanthionine from other compounds of this class.<sup>655</sup>

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## CHAPTER 5.

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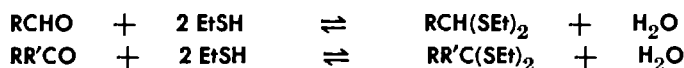
# Mercaptals and Mercaptoles

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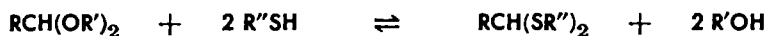
### Introduction

In the mercaptals,<sup>7a</sup> which correspond to the acetals,  $\text{RCH}(\text{OR}')_2$ , the carbonyl oxygen of an aldehyde is replaced by two  $-\text{SR}$  groups. The mercaptoles<sup>7a</sup> are similarly related to ketones but here the oxygen analogs are scarcely known. Mercaptans, in the presence of an acid catalyst, react with ketones as well as with aldehydes though less vigorously:

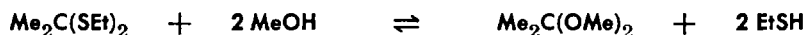


It is well to write both reactions as reversible, though the equilibrium is far to the right in both cases probably even further to the right for the mercaptals than for the mercaptoles.<sup>147</sup>

In chapter 2, Volume I, it was shown that mercaptans are far less effective in the esterification of acids than are the alcohols but in their reactions with aldehydes and ketones the reverse is true. Mercaptans displace alcohols from acetals: 9, 84, 85, 86a, 119, 120, 138a, 143



Boron trifluoride etherate is a catalyst for this reaction.<sup>28, 34</sup> This reaction is, of course, reversible and its completeness will depend on various factors, one of the most important of which is the relative volatility of the alcohol and mercaptan. In fact a practical method of making the oxygen derivatives of ketones is to heat a mercaptole, with an alcohol and an acid catalyst, under a column:<sup>108, 109</sup>



A more volatile mercaptan distills out. In the presence of a catalyst there is interchange between thiols and mercaptals or mercaptoles.<sup>111.5</sup>

### Hemimercaptals and Hemimercaptoles



The reactions, as written above for the formation of mercaptals and mercaptoles from a mercaptan and an aldehyde or ketone, represent the starting materials and the final products. They do not take account of intermediate steps. Physical measurements show that some combination takes place when an alcohol and an aldehyde are mixed:



The products are known as hemiacetals. In general they are unstable and cannot be isolated. The addition products of water and aldehydes are of the same sort:



Chloral hydrate,  $\text{Cl}_3\text{CHO} \cdot \text{H}_2\text{O}$ , and alcoholate,  $\text{Cl}_3\text{CHO} \cdot \text{EtOH}$ , should be written  $\text{Cl}_3\text{CH}(\text{OH})_2$  and  $\text{Cl}_3\text{CH}(\text{OH})\text{OEt}$ . They are exceptionally stable. The stable forms of the thioaldoses are usually cyclic hemimercaptals.

The tendency of mercaptans to unite with aldehydes is even stronger than that of alcohols:



This is evidenced by the evolution of heat when acetaldehyde and ethanethiol are mixed.<sup>55a</sup> The location of the equilibrium and the stability of the hemimercaptal are conditioned by the natures of the aldehyde and of the mercaptan. The formation

of hemimercaptoles is similar but usually does not go so far. Hemimercaptals,  $\text{RCH}(\text{OH})\text{SR}'$ , are placed with other hydroxy-sulfides in the property list, chapter 7, Volume II.

Hemithioformals have been isolated in approximate purity. Only their densities have been determined,  $\text{EtSCH}_2\text{OH}$  d 14/4 1.070,  $\text{PrSCH}_2\text{OH}$  d 14/4 1.018, *i*- $\text{AmSCH}_2\text{OH}$  d 14/4 0.924, and  $\text{PhSCH}_2\text{OH}$  d 14/4 1.182.<sup>96</sup> Formaldehyde unites with cysteine<sup>64</sup> and with ethyl mercaptan with evolution of heat.<sup>55a</sup>

Chloral forms stable hemimercaptals,  $\text{Cl}_3\text{CH}(\text{OH})\text{SR}$ , corresponding to the alcoholates.<sup>52.5, 103, 104.7</sup> The dissociation constants for the methyl, ethyl, butyl, allyl, and phenyl compounds have been determined.<sup>79, 110</sup>

Methylglyoxal forms hemimercaptals,  $\text{MeCOCH}(\text{OH})\text{SR}$ .<sup>66, 156, 182</sup> Phenyl- and thienyl-glyoxals,  $\text{PhCOCHO}$  and  $\text{C}_4\text{H}_3\text{S}\cdot\text{COCHO}$ , form particularly stable hemimercaptals with a variety of mercaptans. These may be recrystallized and have definite melting points, several as high as  $90^\circ$ .<sup>88c, 89, 161</sup> Glyoxylic and pyruvic acids combine with phenyl and benzyl mercaptans.<sup>161</sup> Pyruvic acid,  $\text{MeCOCOOH}$ , though a ketone, is active in combining with mercaptans.<sup>23, 141</sup> Heat is evolved when it unites with thioglycolic acid to form a crystalline compound.<sup>21, 54</sup>

Thioglycolic acid and its anilide,  $\text{HSCH}_2\text{CONHPh}$ , form addition products with aldehydes which are regarded as hemimercaptals. Cysteine gives similar compounds.<sup>156</sup> Glutathione and thiolactic acid appear to be constituents of hemimercaptals which serve as substrates for certain enzymes.<sup>14</sup> Hemimercaptals are formed by the addition of mercaptans to phenanthraquinone, chrysoquinone, and acenaphthaquinone. These are well crystallized compounds.<sup>151</sup> Heat is evolved when ethylene mercaptan is mixed with an aldehyde.<sup>47a</sup> Opianic acid and *p*-nitrophenyl mercaptan give 3-(*p*- $\text{NO}_2\text{C}_6\text{H}_4\text{S}$ )-6,7-dimethoxyphthalide, a lactone of the hemimercaptal.<sup>49b</sup> The same mercaptan forms a hemimercaptal with trichloroacetaldehyde, but only by the aid of hydrogen chloride. The mercaptal is not formed.<sup>49c</sup> Benzylpenilloaldehyde forms a hemimercaptal with thiophenol, m.  $87^\circ$ .<sup>26</sup>

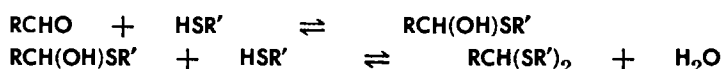
The reactions above for the formation of hemimercaptals are all written as reversible. Even the most stable of them are easily hydrolyzed to the original aldehydes and mercaptans.<sup>7a</sup>

The grouping  $-\text{N}\cdot\text{CH}(\text{OH})\text{S}-$  is present in the pseudo-bases derived from thiazolium salts.<sup>107, 179</sup>

The well known addition product of carvone and hydrogen sulfide, which melts at  $190^{\circ}$ , probably contains the group,  $:C(OH)SH$ , and may be put alongside of the hemimercaptoles.<sup>6, 75, 173</sup> The addition product of benzaldehyde and hydrogen disulfide, which has been formulated as  $PhCH(OH)SS(HO)CHPh$ , may be mentioned here.<sup>27</sup> The recently discovered *gem*-dithiols,  $RCH(SH)_2$ , which have been taken up in chapter 1, Volume I, may be placed with  $RCH(OH)SH$ .<sup>28</sup>

### Mercaptals

The formation of a mercaptal must go in two stages:

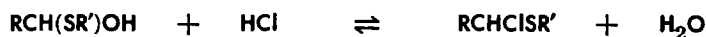


As stated above, the first reaction takes place on simple mixing of the reactants. The second requires an acid catalyst. Similar statements can be made about the formation of mercaptoles. Hydrogen chloride is the commonly used catalyst. It is passed into the mixture of equivalent amounts of aldehyde and mercaptan at room temperature. The speed of the reaction depends on the reactivities of both reactants. With some mixtures a single bubble of the gas is sufficient to bring about the reaction and cooling may be necessary to moderate it. With others, saturation with the gas is necessary, and with some the addition of zinc chloride is required.<sup>7a</sup> The reaction may be practically instantaneous or may take several hours or days. The separation of water shows its progress. As the water that is formed may not separate out well on account of small density differences, it is convenient to add some zinc chloride to collect it. The non-aqueous layer is separated and resaturated with hydrogen chloride and left overnight. It is then dried with zinc chloride and fractionated.<sup>55a, 130</sup>

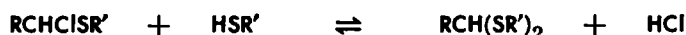
A zinc mercaptide and an aldehyde are dissolved in alcohol and the solution saturated with hydrogen chloride.<sup>142</sup>

Formaldehyde and other water-soluble aldehydes react satisfactorily in aqueous solution.

When there is no excess of mercaptan the hemimercaptal reacts with the hydrogen chloride:<sup>17</sup>



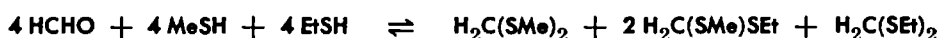
The  $\alpha$ -chloroalkyl sulfide is very reactive with water, alcohols, or mercaptans. It may be considered an intermediate in the formation of mercaptals:<sup>18,5</sup>



The chloromethyl sulfides,  $\text{RSCH}_2\text{Cl}$ , from formaldehyde are the best known of this class.<sup>181</sup> See chapter 4, Volume II.

Formaldehyde reacts particularly well with mercaptans. Many mercaptals,  $\text{H}_2\text{C(SR)}_2$ , have been made.<sup>56, 96, 146, 164</sup> The double ended aldehyde glyoxal reacts with four molecules of a mercaptan to give double mercaptals such as  $(\text{PhS})_2\text{CH}\cdot\text{CH}(\text{SPh})_2$ .<sup>166</sup> 2,3-Dichloro-1,4-dioxane reacts with mercaptans giving the same products as glyoxal.<sup>126</sup>

A mixture of mercaptans gives an equilibrium of all of the possible mercaptals:<sup>65b</sup>



If this mixture is fractionated the first thing to go over will be the dimethyl mercaptal, which is the most volatile. If the catalyst is still present the equilibrium will be readjusted continuously during the distillation with the result that the mixed mercaptal will disappear. There will be only two fractions, the low boiling dimethyl thioformal and the high boiling diethyl compound. If, however, the catalyst is completely eliminated before distillation there will be three fractions, the middle one being the mixed mercaptal.

The mixed mercaptal can be obtained through the intermediate chloromethyl ethyl sulfide:



This is treated with sodium methyl mercaptide:



The mixed thioformal can be purified by distillation.<sup>18, 20</sup>

This chloride reacts also with sodium ethylate:<sup>20</sup>



The product is a monothioformal. The same compound can be prepared starting with chloromethyl ethyl ether:<sup>175</sup>

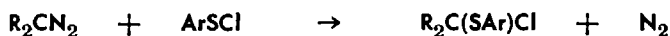


If this is heated in the presence of even a trace of an acid it disproportionates into an equilibrium mixture of formal, monothioformal, and dithioformal. If this mixture is fractionated in the presence of the catalyst, the equilibrium is continuously re-adjusted and only two fractions are obtained, the formal and the dithioformal. Any  $\alpha$ -chloroether reacts similarly with a mercaptan or a sodium mercaptide.<sup>116</sup> A monothioacetal can be formed by the addition of a mercaptan to a vinyl ether with acid catalyst: <sup>32b, 90, 157.5</sup>



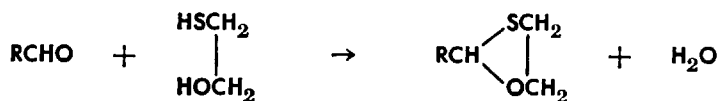
When formaldehyde, water, an alcohol, a mercaptan, and hydrochloric acid are present in a mixture there is a mobile equilibrium among all possible products,  $\text{H}_2\text{C}(\text{OH})\text{SR}$ ,  $\text{H}_2\text{C}(\text{SR})_2$ ,  $\text{H}_2\text{C}(\text{OH})\text{OR}'$ ,  $\text{H}_2\text{C}(\text{OR}')_2$ ,  $\text{H}_2\text{C}(\text{OR}')\text{Cl}$ ,  $\text{H}_2\text{C}(\text{SR})\text{Cl}$ ,  $\text{H}_2\text{C}(\text{OR}')\text{SR}$ . The relative proportions of these depend on the concentrations of the original reactants and the equilibria in the several reactions. If one of the products separates out, on account of volatility or insolubility, the equilibrium is disturbed and more of that product will be formed.

The chlorides,  $\text{R}_2\text{C}(\text{SR})\text{Cl}$ , which may be intermediate products in the formation of mercaptoles are not well known. An aromatic sulfenyl chloride reacts with an aliphatic diazo compound to give a haloalkyl aryl sulfide: <sup>153</sup>



Aromatic compounds of this type, such as  $\text{Ph}_2\text{C}(\text{SPh})\text{Cl}$ , are unstable to heat. This chloride goes into a mixture of the mercaptole,  $\text{Ph}_2\text{C}(\text{SPh})_2$ , and stilbene when it is shaken with mercury. <sup>154</sup>

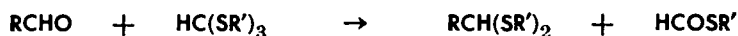
Mercaptoethanol may give a straight mercaptal,  $\text{RCH}(\text{SCH}_2\text{CH}_2\text{OH})_2$ ,<sup>57</sup> or a cyclic mixed acetal-mercaptal: <sup>88b</sup>



3-Chloroallyl mercaptan and acetaldehyde give  $\text{CH}_3\text{CH}(\text{SCH}_2\text{CH:CHCl})_2$ .<sup>31</sup> Sulfide aldehydes,  $\text{PhCH}_2\text{SCH}_2\text{CHO}$  and  $\text{EtSCH}_2\text{CH}_2\text{CHO}$ , react regularly with mercaptans.<sup>58, 138a</sup>



Trithio-orthoformic esters,  $\text{HC}(\text{SR})_3$ , may serve as sources of  $\text{RS}-$  groups for making mercaptals: <sup>32a, 124</sup>

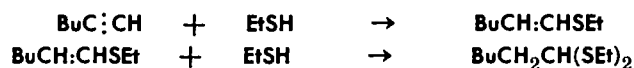


Mercaptals and mercaptoles can be made directly from Bunte salts. <sup>65a, 165, 176</sup> This avoids the handling of the odorous mercaptan in the manufacture of sulfonal. <sup>46a</sup>

Mercaptals are produced by adding mercaptans to acetylene: <sup>131</sup>

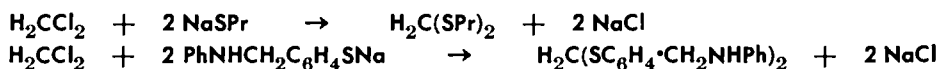


With butyl acetylene the addition goes in two stages: <sup>82</sup>

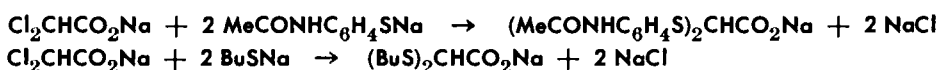


The mercaptals from higher dimercaptans, such as hexamethylene and decamethylene are linear polymers. <sup>104, 104.3, 104.5</sup> The reaction products of butyl and benzyl mercaptans with spruce lignin may be mercaptals. <sup>22</sup>

Methylene halides can be used with alkali and simple <sup>5, 19a, 55a, 61, 91, 92a, 159, 167</sup> or complex <sup>12</sup> mercaptans:

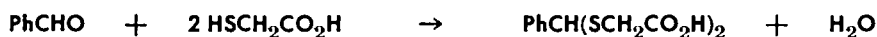


Dichloroacetic acid, <sup>12</sup> its ester, <sup>19b</sup> and amide <sup>42</sup> have been used similarly:



Chloroform and even carbon tetrachloride give the same products as methylene chloride, the extra chlorine serving to oxidise a part of the mercaptide to the disulfide. <sup>7c</sup>

Many mercaptals have been made from thioglycolic acid, which is sufficiently acid to serve as its own catalyst: <sup>21, 72b, 74</sup>



$\beta$ -Mercaptopropionic acid has been used with a variety of aldehydes. <sup>73c, 165</sup> There are meso and racemic forms of the mercaptal from formaldehyde and thiolactic acid. <sup>53</sup>

The mercaptals from thioglycolic and  $\beta$ -mercaptopropionic acids have been proposed as suitable derivatives for the identifi-

cation of aldehydes<sup>135, 142</sup> and ketones.<sup>135</sup> Many of them have satisfactory melting points. Their neutralization equivalents furnish further identification.<sup>135</sup> As will be seen later, mercaptals are particularly useful for the isolation and characterization of sugars. The preparation and cleavage of a number of thioglycolic acid derivatives have been studied with a view to their use in identifying and estimating the decomposition products of lignin, such as propionic and protocatechuic aldehydes, vanillin, veratraldehyde, phenylacetaldehyde, phenylpropionaldehyde, pyruvic, and acetoacetic acids.<sup>72a</sup>

Three molecules of benzaldehyde react with two of 4-amino- $\alpha$ -thionaphthol to form a Schiff's base-mercaptal,  $\text{PhCH}(\text{SC}_{10}\text{H}_6\text{N}:\text{CHPh})_2$ <sup>183</sup>

The mercaptals and mercaptoles from the reactions of aldehydes and ketones with ethylene, trimethylene, and *o*-phenylene dimercaptans are cyclic sulfides and have been taken up in chapter 1. Those from thioglycolic and other mercaptoacids are bis-sulfide acids and are in chapter 3.

### Mercaptoles

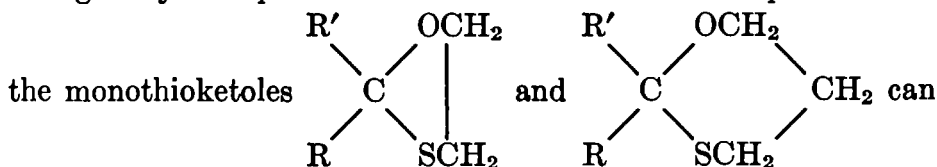
These have been prepared in considerable variety.<sup>39</sup> Ketones are not as reactive as aldehydes of the same class. Thus, acetone and benzophenone are inferior in reactivity to acetaldehyde and benzaldehyde. Ketones having two large alkyls, particularly if these have branches near the carbonyl group, are sluggish. Methyl ketones,  $\text{MeCOR}$ , are reactive, even up to methyl nonyl.<sup>95</sup> Cyclopentanone<sup>130, 174</sup> and cyclohexanone<sup>69, 129a, 130, 174</sup> are as reactive as acetone. With ethyl phenyl ketone<sup>145</sup> and with benzophenone<sup>7b, 113, 145</sup> zinc chloride must be added. Three molecules of ethyl mercaptan react with benzoin but one is split off leaving  $\text{PhC}(\text{SEt}):\text{C}(\text{SEt})\text{Ph}$ .<sup>122b</sup> When a mercaptan reacts with formylacetone the final product is  $\text{MeC}(\text{SR}):\text{CHCH}(\text{SR})_2$ , which may result from the loss of a molecule of the mercaptan from  $\text{MeC}(\text{SR})_2\text{CH}_2\text{CH}(\text{SR})_2$  or a molecule of water from the hemimercaptole,  $\text{MeC}(\text{SR})(\text{OH})\text{CH}_2\text{CH}(\text{SR})_2$ .<sup>42.5</sup> Perhaps water is lost from a bezoin hemimercaptole in the above reaction.

The reactivity of the mercaptan decreases somewhat as the molecular weight increases.<sup>121c</sup> *n*-Butyl mercaptan is active.<sup>177</sup> Thiophenol is less reactive than the aliphatic mercaptans.<sup>122a</sup>

Ketosulfides,<sup>2c</sup>  $\alpha$ -chloroketones,<sup>123</sup> hydroxy-ketones,<sup>40</sup> and iso-

nitrosoacetone <sup>121a</sup> react normally with mercaptans to give the corresponding mercaptoles.  $(\text{EtSCH}_2)_2\text{CO}$  <sup>137</sup> and 2-acetfurane <sup>88a</sup> also react normally with mercaptans.

As the formation of a mercaptole is a reversible reaction, interchange may take place between a ketone and a mercaptole. Thus



be made by displacing acetone by a higher ketone.<sup>41.5</sup>

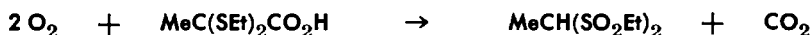
9,9-Dichlorofluorene reacts with thiophenol in benzene solution.<sup>154</sup> The benzyl mercaptoles can be made from 9-fluorenone.<sup>137.5</sup>

There has been considerable interest in the mercaptoles from ketosteroids.<sup>13, 68, 69, 80, 81, 97, 115, 128, 137.7a</sup>

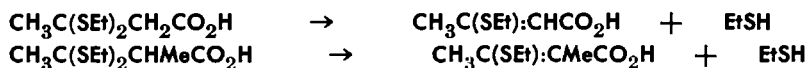
In a ketoacid the reactivity of the carbonyl group is influenced by its distance from the carbonyl and by the presence of substituents on adjacent carbon atoms.

Mercaptoles can be made by replacing the active methylene of malonic and acetoacetic esters by alkylmercapto groups.<sup>4.5</sup>

Heat is evolved and a hemimercaptole is formed when pyruvic acid is mixed with a mercaptan. With more of the same mercaptan and a catalyst this goes into the mercaptole.<sup>45</sup> With a different mercaptan some of the mixed mercaptole is obtained.<sup>122d</sup> In making a mercaptole from pyruvic acid and a mercaptan, if the mixture is not cooled, carbon dioxide is eliminated leaving a mercaptal.<sup>45</sup> When pyruvic mercaptoles are oxidised the carboxyl is lost: <sup>45, 121b, 122d</sup>



Acetoacetic ester forms mercaptoles readily <sup>2b, 7c, 45, 121b, 121e</sup> but the presence of an alkyl in the methylene group cuts down the reactivity. When there are two alkyls in this group only the lower mercaptans react and the products are unstable.<sup>121e</sup> The free acids lose half of the mercaptan: <sup>121b</sup>



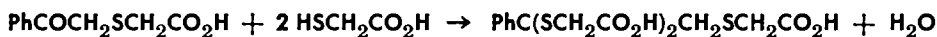
Similarly  $\beta$ -ketoglutaric acid forms mercaptoles readily and the free acids lose mercaptan: <sup>2b, 121b</sup>



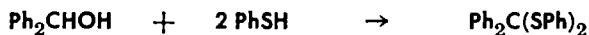
As will be shown later on, the loss of half of the mercaptan is a general reaction but in these cases it takes place under unusually mild conditions.

The reactivity of a ketone is diminished by the proximity of a double bond to the carbonyl, or rather by the —SR group which is present after the addition of the mercaptan across the double bond.<sup>121d, 122c</sup> Some unsaturated ketones react with three molecules of a mercaptan, one for the double bond and two for the carbonyl.<sup>122c, 140</sup> When a carbonyl group is between two double bonds two molecules of mercaptan are added but no mercaptole is formed.<sup>122e</sup> Benzoquinone, which may be formulated as belonging to this class, reacts as a monoketone. There is no addition of the mercaptan.<sup>129b</sup>

A mercaptoacid may react with a keto-acid: <sup>73a, 92b</sup>



In concentrated sulfuric acid benzhydrol and a mercaptan give a mercaptole: <sup>15</sup>



Diketones have been extensively investigated with reference to mercaptole formation. If the two carbonyls are at a distance from each other they react independently. With  $\alpha$ - and  $\beta$ -diketones, dimercaptoles are formed only when the terminal groups are methyls and the intervening group of the  $\beta$ -ketone is methylene. Otherwise only one carbonyl reacts and the other becomes inactive to hydroxylamine and phenylhydrazine, as well as to mercaptans. Thus, we have  $\text{MeC}(\text{SEt})_2\text{C}(\text{SEt})_2\text{Me}$ ,  $\text{MeC}(\text{SEt})_2\text{CH}_2\text{C}(\text{SEt})_2\text{Me}$  and  $\text{MeC}(\text{SCH}_2\text{Ph})_2\text{C}(\text{SCH}_2\text{Ph})_2\text{Me}$ , in contrast to  $\text{MeC}(\text{SEt})_2\text{COEt}$ ,  $2 \text{PhC}(\text{SEt})_2\text{COPh}$  and  $\text{MeC}(\text{SEt})_2\text{CHMe}\cdot\text{COMe}$ . Benzil requires zinc chloride in addition to hydrogen chloride and then only one carbonyl reacts.<sup>11, 121c</sup> It would be of interest to reinvestigate this field using a greater variety of mercaptans such as are now available.

In acetonylacetone the carbonyls are far enough apart to act independently. The dimercaptoles have been prepared from the normal mercaptans methyl to dodecyl.<sup>133, 134</sup> The melting points make an interesting pattern. They show alternation just as if one chain were being lengthened instead of four.

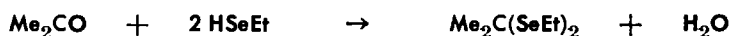
Mercaptoacids, such as thioglycolic, react with ketones as well as with aldehydes but not so readily. The mercaptoles,

$RR'C(SCH_2CO_2H)_2$ , have been mentioned in chapter 3 as bis-sulfide acids. They are considered here as mercaptoles. Thio-glycolic acid has been a favorite mercaptan for the synthesis of mercaptoles in general.<sup>21, 72a, 73d, 165</sup> The ethyl ester<sup>158</sup> and the anilide<sup>10, 62</sup> function as the acid.  $\beta$ -Mercaptopropionic acid also has been used frequently.<sup>73c</sup>

In their reactions with both aldehydes and ketones,  $\beta$ -chloro-ethyl,<sup>37</sup> *p*-nitrophenyl,<sup>49a, 49b, 59</sup> and 3-thienyl<sup>24, 25</sup> mercaptans,  $ClCH_2CH_2SH$ ,  $p\text{-NO}_2C_6H_4SH$ , and  $3\text{-C}_4H_3S\text{-SH}$ , behave as ordinary mercaptans. The same is true of thiofurfuryl alcohol,  $C_4H_3O\cdot CH_2SH$ .<sup>30.5</sup>

An aminomercaptal<sup>105</sup> and an aminomercaptole<sup>121a</sup> have been made by way of phthalimide. Quite a number of these have been made from cysteine which reacts normally with aldehydes and ketones.<sup>1, 106, 117, 156</sup> The aminomercaptal,  $MeCH(NH_2)CH\text{-(SEt)}_2$  has been prepared by displacing alcohol from the corresponding acetal by mercaptan.<sup>9</sup>

Selenomercaptans condense with ketones in the presence of hydrogen chloride:<sup>157</sup>



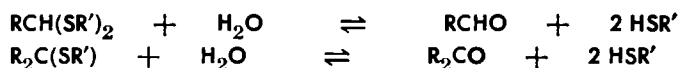
### Reactions

In this section mercaptals and mercaptoles are taken up together, though some of the reactions relate more specifically to the one than to the other.

The reactions of mercaptals are said to be dependent on the possibility of setting up valency structures which involve the expansion of the valency shell of the sulfur atom.<sup>138b</sup> The reactions which involve the breaking of a carbon-sulfur bond have been reviewed.<sup>169</sup>

In solution in acetic acid containing hydrogen chloride, formaldehyde displaces ketones and other aldehydes and may react further with aromatic formals so formed.<sup>170</sup>

The acid hydrolysis of mercaptals and mercaptoles is simply the reversal of the reactions by which they are formed: <sup>7a</sup>



If mercuric chloride, which reacts with the mercaptans to form stable insoluble mercaptides, is present the hydrolysis goes to completion.<sup>9, 41, 72a, 73d, 73e</sup> Mercaptoles are cleaved in the pres-

ence of cadmium chloride but mercaptals are not.<sup>72a</sup> As will be seen in the next section, much use has been made of this reaction in the sugar group.

The halfway mercaptole  $\text{MeC}(\text{SEt})_2\text{CH}_2\text{COMe}$ , from acetylacetone, when treated with sodium ethoxide, gives a crystalline sodium derivative.<sup>99</sup>

Acting as a *bis*-sulfide, a mercaptal forms a *bis*-sulfonium compound with ethyl iodide:

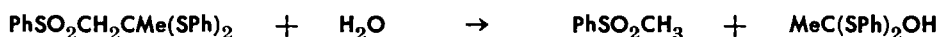


Iodoform may be added to this.<sup>46b</sup>

Both mercaptals and mercaptoles as such are stable to alkali<sup>60</sup> but hydrolysis does occur when another part of the molecule is subject to attack.<sup>2a, 118</sup> This is illustrated by the alkaline hydrolysis of a mercaptole containing a sulfone group:<sup>118</sup>



The first step may be:



Or, to look at it another way, the ketone,  $\text{PhSO}_2\text{CH}_2\text{COMe}$ , from which the mercaptole is derived, is subject to alkaline hydrolysis.

It has been noted above that the mercaptoles of acetoacetic<sup>121b</sup> and of  $\beta$ -ketoglutaric<sup>2a</sup> acids lose half of the mercaptan spontaneously. Only a few of the lower mercaptals or mercaptoles can be distilled, even at reduced pressures. Under atmospheric pressure mercaptan is split out:<sup>34, 163, 178</sup>



Hydrogen chloride and zinc chloride facilitate this reaction.<sup>29</sup> This is a convenient way to make olefinic sulfides.<sup>172</sup> Heating with zinc chloride causes more drastic decomposition:<sup>163</sup>



The decomposition has been known to go in a different direction:<sup>8</sup>

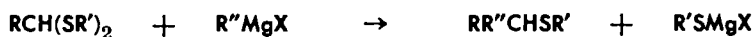


The thioacetone was not isolated but its presence was inferred from the odor, which is said to surpass all other odors in intensity.<sup>8</sup> Fortunately other workers have not been able to repeat this.<sup>163</sup> Aryl mercaptoles do decompose in this way:<sup>149, 150, 152</sup>



By a series of reactions, starting with sodium malonic ester and carbon disulfide, the acid,  $(\text{MeS})_2\text{C}:\text{C}(\text{CO}_2\text{H})_2$ , is obtained. The loss of carbon dioxide leaves a ketene mercaptal,  $\text{H}_2\text{C}:-\text{C}(\text{SMe})_2$ .<sup>86b, 87</sup>

A Grignard reagent removes one  $-\text{SR}$  group:

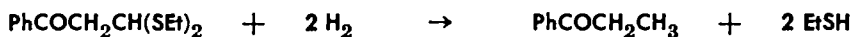


The product is an alkyl sulfide.

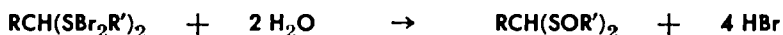
Raney nickel removes the  $-\text{SR}$  groups from mercaptals and mercaptoles. In most cases hydrogen atoms are put in their places.<sup>13, 68, 114, 137.7b, 180</sup> Thus 3-cholestanone is converted to a mercaptole and this is treated with Raney nickel to give cholestane.<sup>13</sup> A mercaptal of benzaldehyde is converted to stilbene.<sup>70</sup> <sup>71</sup> Sodium removes  $-\text{SPh}$  from  $\text{Ph}_2\text{C}(\text{SPh})_2$  leaving tetraphenylethylene,  $\text{Ph}_2\text{C}:\text{CPh}_2$ .<sup>148</sup> Sodium in liquid ammonia converts cyclohexanone dibenzyl mercaptole into cyclohexyl mercaptan and benzylcyclohexane.<sup>162.5</sup> Hydrogenation over molybdenum sulfide removes one methylmercapto group and then the other from cyclohexanone dimethyl mercaptole:<sup>31.5</sup>



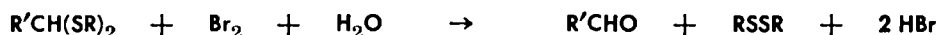
Hydrogenolysis may split a mercaptal:<sup>83</sup>



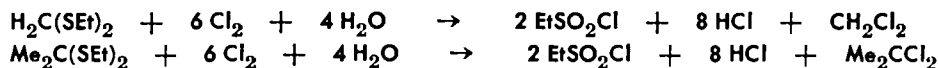
Chlorine, bromine, and iodine may be added to the two sulfur atoms. Hydrolysis of these addition products gives *bis*-sulfoxides:<sup>47b, 55b</sup>



These *bis*-sulfoxides have been obtained by oxidation with hydrogen peroxide<sup>18, 56</sup> and with permanganate.<sup>4</sup> In the presence of water, bromine converts a mercaptal into the aldehyde and the disulfide:<sup>61.5</sup>

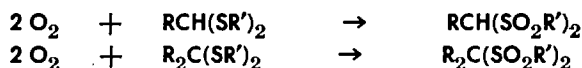


This is the basis for titrating a mercaptal with bromide-bromate.<sup>61.7</sup> Chlorination may give the sulfone chloride corresponding to the mercaptan:



The sulfone  $\text{Me}_2\text{C}(\text{SO}_2\text{Et})_2$  is not an intermediate since it is stable under the conditions.<sup>94</sup> The explanation seems to be that the mercaptan is liberated by acid hydrolysis and is then chlorinated.

The best known reaction of both mercaptals and mercaptoles is their oxidation to the *bis*-sulfones:



In many cases the mercaptals and mercaptoles have been prepared only as intermediates and not characterized as such. The oxidation products are often better known than the products from which they are derived. The *bis*-sulfones are more apt to be solids and hence easier to characterize. The oxidising agent most often used has been potassium permanganate.<sup>2b, 3, 7c, 45, 47b, 55a, 56, 95, 118, 121a, 121c, 122a, 122d, 129a, 145, 163, 174</sup> Chromate,<sup>177</sup> nitric acid,<sup>47b, 177</sup> persulfate,<sup>73b, 73e</sup> and phthalic monoperacid<sup>19b</sup> have been employed. Hydrogen peroxide has come into extensive use.<sup>4, 12, 18, 42, 65b, 138a</sup> Electrolytic oxidation may stop at the *bis*-sulfoxide or at the *bis*-sulfone or go on to ethanesulfonic acid.<sup>51</sup> The electrolytic oxidation product from  $\text{Me}_2\text{C}(\text{SEt})_2$ , which was formerly supposed to be  $\text{Me}_2\text{C}(\text{SOEt})_2$ , has been found to be  $\text{EtSO}_2\text{SEt}$ .<sup>50</sup> The oxidation of  $\text{PhCH}(\text{SCH}_2\text{COOK})_2$  by potassium persulfate gives the lactone of  $\alpha$ -hydroxybenzylmercaptoacetic acid.<sup>73b, 73e</sup>

Though it does not belong to the chemistry of bivalent sulfur, to which this work is restricted, a striking property of these *bis*-sulfones may be mentioned. That is their stability. Where there are two carbonyl groups on a single carbon atom, as in acetoacetic ester, hydrolysis takes place readily, but when the carbonyls are on adjacent carbon atoms there is no hydrolysis. With *bis*-sulfones it is just the reverse;  $\text{RSO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{R}$  are readily hydrolyzed while  $\text{RSO}_2\text{CH}_2\text{SO}_2\text{R}$  are not. Malonic acid is unstable while  $\text{H}_2\text{C}(\text{SO}_3\text{H})_2$  is stable. A carboxyl on the same carbon atom as a sulfone group, as in  $\text{RSO}_2\text{CH}_2\text{COOH}$ , is easily eliminated.

### Uses

Forming mercaptals has been recommended as a way of getting undesirable mercaptans out of hydrocarbon distillates.<sup>16, 76, 98, 127,</sup>



<sup>132</sup> On the other hand this reaction may be employed to get aldehydes or ketones out of mixtures.<sup>155</sup>

The mercaptals from acetaldehyde and *t*-butyl and *t*-dodecyl mercaptans are claimed as selective solvents for separating olefins and paraffins.<sup>33</sup>

Several mercaptals are mothproofing agents.<sup>63, 102</sup> Certain mercaptals are pickling inhibitors.<sup>93</sup> Acetone mercaptoles are claimed as stabilizers and antioxidants.<sup>38, 111, 112, 139</sup> Derivatives of sugars are specially mentioned.<sup>160</sup> One is a catalyst for phenol-ketone condensations<sup>77</sup> and several are therapeutic agents.<sup>136</sup>

It is claimed that useful products are obtained by condensing mercaptals with oxo compounds.<sup>144</sup> Mercaptals and mercaptoles from 3-thiophenethiol are said to be additives for petroleum fractions.<sup>24</sup> The mercaptole from thioglycolic acid and levulinic acid is of value in the regulation of plant growth.<sup>112.5</sup>

Certain mercaptals have been claimed as dye intermediates,<sup>44, 86a</sup> others as waxes or wetting agents<sup>39</sup> and still others as lacquer constituents.<sup>43</sup> The reaction product of a mercaptan with formyl-acetone is claimed as an intermediate for making a cyanine dye.<sup>42.5</sup>

Mercaptals from chloral are said to be useful in extreme pressure lubricants.<sup>35</sup> Mercaptals from salicylaldehyde are claimed as useful in coatings for textiles and paper and in plasticizers for rubber.<sup>171</sup> The mercaptole,  $\text{Me}_2(\text{SC}_6\text{H}_4\text{Cl-}p)_2$ , is claimed as a miticide.<sup>78</sup>

### Physical Properties

Here, as in other chapters, the property list shows what compounds have been made and who made them. The remarks in the introduction to the tables in chapter 1, Volume I apply here also with equal force.

The thioformals,  $\text{H}_2\text{C}(\text{SR})_2$ , are in the sulfide table in chapter 3, Volume II, mercaptals and mercaptoles of mercaptoacids are with sulfide acids in chapter 3 and cyclic compounds are in chapter 1 on cyclic sulfides.

The parachors of mercaptoles are normal.<sup>101</sup> Ultraviolet spectra have been determined.<sup>48a</sup>

### Mercaptals

$\text{MeCH}(\text{SMe})_2$ , b.  $156-8^\circ$ .<sup>65b</sup>

$\text{MeCH}(\text{SEt})_2$ ,  $b_{12} 77^\circ$ ,<sup>32b</sup>  $b_{19} 73^\circ$ ,<sup>131</sup>  $b_{758} 186-9^\circ$ ,<sup>124</sup> b.  $185-7^\circ$ ; <sup>55a</sup>,

- <sup>100</sup> d 26/4 0.9425, d 27/4 0.9550; n 26/D 1.4984, n 28/D 1.4985.<sup>124</sup>
- MeCH(SPr)<sub>2</sub>, b<sub>13</sub> 116°; d 23.5/4 0.9539; n 23.5/D 1.4950.<sup>124</sup>
- MeCH(SBu)<sub>2</sub>, b<sub>3</sub> 105°; d °/4 0.9397, d 25/4 0.9245; n 20/D 1.4900.<sup>177</sup>
- MeCH(SBu-*t*)<sub>2</sub>, b<sub>3</sub> 85–92°,<sup>162</sup> b<sub>60</sub> 135–6°; d<sub>24</sub> 0.910; n 20/D 1.4858.<sup>33</sup>
- MeCH(SC<sub>12</sub>H<sub>25</sub>-*t*)<sub>2</sub>, d<sub>24</sub> 0.920; n 20/D 1.4928.<sup>33</sup>
- MeCH(SMe)SPh, b<sub>10</sub> 140–5°.<sup>65b</sup>
- MeCH(SCH<sub>2</sub>CH<sub>2</sub>OEt)<sub>2</sub>, b<sub>4.5</sub> 131–4°; d 20/4 1.0120; n 20/D 1.4893.<sup>125</sup>
- MeCH(SCH<sub>2</sub>CH<sub>2</sub>OBu)<sub>2</sub>, b<sub>3.5</sub> 166.5–9°; d 20/4 0.9702; n 20/D 1.4814.<sup>125</sup>
- MeCH(SCH<sub>2</sub>CH:CHCl)<sub>2</sub>, b<sub>13</sub> 162–4°.<sup>31</sup>
- MeCH(SC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-*p*)<sub>2</sub>, m. 83°; diAc., m. 193°.<sup>136</sup>
- MeCH(SCH<sub>2</sub>Ph)<sub>2</sub>, b<sub>5</sub> 200–5°,<sup>56</sup> b<sub>0.5</sub> 168°.<sup>131</sup>
- MeCH(SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*p*)<sub>2</sub>, m. 32°.<sup>142</sup>
- MeCH(SC<sub>4</sub>H<sub>3</sub>O-2)<sub>2</sub>, b<sub>13</sub> 165–7°.<sup>30.5</sup>
- EtCH(SET)<sub>2</sub>, b<sub>7</sub> 70–5°,<sup>28</sup> b. 196–200°;<sup>55a</sup> d 25/4 0.954; n 25/d 1.4969.<sup>28</sup>
- EtCH(SC<sub>4</sub>H<sub>3</sub>O-2)<sub>2</sub>, b<sub>13</sub> 185–7°.<sup>30.5</sup>
- PrCH(SBu-*t*)<sub>2</sub>, b<sub>4</sub> 107–110°.<sup>162</sup>
- PrCH(SC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*p*)<sub>2</sub>, m. 87°.<sup>49a</sup>
- PrCH(SC<sub>4</sub>H<sub>3</sub>S-3)<sub>2</sub>, b<sub>2</sub> 173–6°.<sup>24, 25</sup>
- PrCH(SC<sub>4</sub>H<sub>3</sub>O-2)<sub>2</sub>, b<sub>3</sub> 180–1°.<sup>30.5</sup>
- i*-PrCH(SET)<sub>2</sub>, b. 200–10°.<sup>55a</sup>
- i*-BuCH(SC<sub>4</sub>H<sub>3</sub>O-2)<sub>2</sub>, b<sub>3</sub> 192–3°.<sup>30.5</sup>
- PhCH(SBu)<sub>2</sub>, b<sub>4</sub> 167°; d 0/0 1.0180, d 25/4 0.9970; n 20/D 1.4445.<sup>177</sup>
- PhCH(SBu-*t*)<sub>2</sub>, m. 146.5°.<sup>162</sup>
- PhCH(SPh)<sub>2</sub>, m. 51°.<sup>111.5</sup>
- PhCH(SCH<sub>2</sub>Ph)<sub>2</sub>, m. 61°,<sup>176</sup> 60°,<sup>111.5</sup> 63°.<sup>18.5</sup>
- PhCH(SC<sub>4</sub>H<sub>3</sub>S-3)<sub>2</sub>, b<sub>1</sub> 100°.<sup>24</sup>
- PhCH(SCH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, m. 58°.<sup>57</sup>
- PhCH(SCMe<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>, m. 195°.<sup>32.5</sup>
- PhCH<sub>2</sub>CH<sub>2</sub>CH(SC<sub>4</sub>H<sub>3</sub>S-3)<sub>2</sub>, b<sub>1</sub> 100°.<sup>24</sup>
- p*-MeC<sub>6</sub>H<sub>4</sub>CH(SC<sub>6</sub>H<sub>4</sub>Me-*p*)<sub>2</sub>, m. 72°.<sup>170</sup>
- p*-Me<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>CH(SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*p*)<sub>2</sub>, m. 84°.<sup>142</sup>
- CH<sub>2</sub>:C(SMe)<sub>2</sub>, b<sub>10</sub> 80°.<sup>87</sup>
- CH:CCH(SET)<sub>2</sub>, b<sub>10</sub> 125°.<sup>86</sup>
- CH<sub>2</sub>:CHCH(SET)<sub>2</sub>, b<sub>9</sub> 83°.<sup>138a</sup>

$\text{MeCH:CHCH(SET)}_2$ ,  $b_{24}$  128°,  $b_{10}$  116°;  $n$  20/D 1.5256.<sup>67</sup>  
 $\text{PhCH:CHCH(SCH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)_2$ ,  $m$ . 140°. <sup>142</sup>  
 $2\text{-C}_4\text{H}_3\text{O}\cdot\text{CH(SC}_4\text{H}_3\text{O-}2)_2$ ,  $b_1$  100°, <sup>24</sup>  $b_3$  210-2°. <sup>80.5</sup>  
 $\text{CHOCH(SCH}_2\text{Ph)}_2$ ,  $m$ . 174°. <sup>145.5</sup>  
 $[\text{CH(SCH}_2\text{Ph)}_2]_2$ ,  $m$ . 68°. <sup>126</sup>  
 $\text{ClCH}_2\text{CH}_2\text{CH(SET)}_2$ ,  $b_{11}$  115-7°. <sup>138a</sup>  
 $\text{HOCH}_2\text{CH}_2\text{CH(SET)}_2$ ,  $b_{11}$  143-5°. <sup>138a</sup>  
 $\text{EtOCH}_2\text{CH}_2\text{CH(SET)}_2$ ,  $b_9$  115°. <sup>138a</sup>  
 $\text{MeOCH}_2\text{CH(OMe)CH(SET)}_2$ ,  $b_8$  129-30°. <sup>138a</sup>  
 $\text{MeOCH(SET)CH}_2\text{CH(SET)}_2$ ,  $b_3$  122-31°;  $n$  25/D 1.5178. <sup>32a</sup>  
 $\text{EtSCH}_2\text{CH}_2\text{CH(SET)}_2$ ,  $b_{0.2}$  87°,  $b_9$  137-9°. <sup>138a</sup>  
 $\text{EtSCHMeCH(SET)}_2$ ,  $b_{0.3}$  100°. <sup>138a</sup>  
 $\text{BuSCHMeCH(SET)}_2$ ,  $b_{0.3}$  114-6°. <sup>138a</sup>  
 $\text{EtSCH:CHCH(SET)}_2$ ,  $b_5$  185-92°,  $b_{10}$  190°. <sup>86</sup>  
 $\text{HSCH}_2\text{CHSHCH(SET)}_2$ ,  $b_{0.5}$  70-110°. <sup>119</sup>  
 $\text{MeCOCH(SMe)}_2$ ,  $b_{0.11}$  94-6°. <sup>19a</sup>  
 $\text{MeCOCH(SET)}_2$ ,  $b_{12}$  110-2°. <sup>19a</sup>  
 $o\text{-HOC}_6\text{H}_4\text{CH(SC}_6\text{H}_4\text{NO}_2)_2$ ,  $m$ . 145°. <sup>49a</sup>  
 $o\text{-HOC}_6\text{H}_4\text{CH(SCH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)_2$ ,  $m$ . 152°. <sup>142</sup>  
 $2,5\text{-Br(HO)C}_6\text{H}_3\text{CH(SC}_6\text{H}_4\text{Me-}p)_2$ ,  $m$ . 97°. <sup>170</sup>  
 $2,3\text{-HO(MeO)C}_6\text{H}_3\text{CH(SBu-}t)_2$ ,  $m$ . 63°. <sup>162</sup>  
 $4,3\text{-HO(MeO)C}_6\text{H}_3\text{CH(SCH}_2\text{Ph)}_2$ ,  $m$ . 102°. <sup>137.5</sup>  
 $4,3\text{-HO(MeO)C}_6\text{H}_3\text{CH(SC}_6\text{H}_4\text{NO}_2\text{-}p)_2$ ,  $m$ . 155°. <sup>49a</sup>  
 $4,3\text{-HO(MeO)C}_6\text{H}_3\text{CH(SC}_6\text{H}_4\text{NH}_2\text{-}p)_2$ ,  $m$ . 152°. <sup>49a</sup>  
 $o\text{-O}_2\text{NC}_6\text{H}_4\text{CH(SPh)}_2$ ,  $m$ . 101°. <sup>170</sup>  
 $m\text{-NO}_2\text{C}_6\text{H}_4\text{CH(SPh)}_2$ ,  $m$ . 65.5°. <sup>170</sup>  
 $m\text{-NO}_2\text{C}_6\text{H}_4\text{CH(SC}_6\text{H}_4\text{Me-}p)_2$ ,  $m$ . 85.5°. <sup>170</sup>  
 $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH(SC}_{18}\text{H}_{37})_2$ ,  $m$ . 55°. <sup>39</sup>  
 $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH(SC}_6\text{H}_4\text{NO}_2\text{-}p)_2$ ,  $m$ . 166°. <sup>59</sup>  
 $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH(SC}_6\text{H}_4\text{NH}_2\text{-}p)_2$ ,  $\text{diAc.}$ ,  $m$ . 223°. <sup>136</sup>  
 $p\text{-NH}_2\text{C}_6\text{H}_4\text{CH(SC}_6\text{H}_4\text{NH}_2\text{-}p)_2$ ,  $\text{triAc.}$ ,  $m$ . 141°. <sup>59</sup>  
 $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CH(SC}_6\text{H}_4\text{NO}_2\text{-}p)_2$ ,  $m$ . 175°. <sup>49a</sup>  
 $\text{MeCH(NH}_2\text{)CH(SET)}_2$ ,  $b_3$  105°;  $\text{picrate}$ ,  $m$ . 154°. <sup>9</sup>

### Mercaptoles

$\text{Me}_2\text{C(SMe)}_2$ ,  $b_{17}$  56°. <sup>36</sup>  
 $\text{Me}_2\text{C(SET)}_2$ ,  $b_{12}$  75°, <sup>50</sup>  $b$ . 190-1°; <sup>7b</sup>  $d$  16/4 0.9496,  $n$  16/D 1.49392. <sup>163</sup>  
 $\text{Me}_2\text{C(SPr)}_2$ ,  $b_5$  81°;  $n$  25/D 1.4888. <sup>28</sup>  
 $\text{Me}_2\text{C(SBu)}_2$ ,  $b_4$  104, <sup>48b</sup> 110°; <sup>177</sup>  $d$  0/0 0.9304, <sup>177</sup>  $d$  21/4 0.9165, <sup>163</sup>  $d$  25/4 0.9188;  $n$  20/D 1.4842, <sup>177</sup>  $n$  21.2/D 1.48645. <sup>163</sup>

- $\text{Me}_2\text{C}(\text{SAm})_2$ ,  $b_2$  109–11°;  $n$  20/D 1.4870.<sup>38</sup>  
 $\text{Me}_2\text{C}(\text{SCet})_2$ ,  $m$ . 53°.<sup>52</sup>  
 $\text{Me}_2\text{C}(\text{SPh})_2$ ,  $m$ . 56°.<sup>7b</sup>  
 $\text{Me}_2\text{C}(\text{SC}_6\text{H}_4\text{Me-}p)_2$ ,  $m$ . 65°.<sup>56</sup>  
 $\text{Me}_2\text{C}(\text{SCH}_2\text{Ph})_2$ ,  $b_5$  195°.<sup>56</sup>  
 $\text{Me}_2\text{C}(\text{SCH}_2\text{CH}_2\text{Cl})_2$ ,  $b_{23}$  52–60°.<sup>37</sup>  
 $\text{Me}_2\text{C}(\text{SCH}_2\text{CH}_2\text{OEt})_2$ ,  $b_7$  134°;  $d$  20/4 1.0026.<sup>168</sup>  
 $\text{Me}_2\text{C}(\text{SC}_6\text{H}_4\text{NO}_2-p)_2$ ,  $m$ . 122°.<sup>59</sup>  
 $\text{Me}_2\text{C}(\text{SC}_6\text{H}_4\text{NHCOMe-}p)_2$ ,  $m$ . 225°.<sup>12, 136</sup>  
 $\text{Me}_2\text{C}(\text{SC}_6\text{H}_4\text{Cl-}p)_2$ ,  $m$ . 51°.<sup>78</sup>  
 $\text{Me}_2\text{C}(\text{SC}_4\text{H}_3\text{S-3})_2$ ,  $b_1$  148–53°.<sup>24, 25</sup>  
 $\text{Me}_2\text{C}(\text{SC}_4\text{H}_3\text{O-2})_2$ ,  $b_3$  170°.<sup>30.5</sup>  
 $\text{MeEtC}(\text{SEt})_2$ ,  $b_{18.5}$  99–100°.<sup>101</sup>  
 $\text{MeEtC}(\text{SC}_6\text{H}_{11})_2$ ,  $b_3$  175–6°;  $n$  22/D 1.5305.<sup>109</sup>  
 $\text{MeEtC}(\text{SC}_4\text{H}_3\text{O-2})_2$ ,  $b_5$  173–4°.<sup>30.5</sup>  
 $\text{Me}(i\text{Pr})\text{C}(\text{SC}_4\text{H}_3\text{O-2})_2$ ,  $b_5$  185–6°.<sup>30.5</sup>  
 $\text{MePhC}(\text{SBu})_2$ ,  $b_3$  167–8°;  $d$  0/4 1.0238,  $d$  25/4 1.0083;  $n$  20/D 1.5535.<sup>177</sup>  
 $\text{MePhC}(\text{SPh})_2$ ,  $m$ . 155°.<sup>28.5</sup>  
 $\text{Me}(\text{C}_4\text{H}_3\text{S-2})\text{C}(\text{SC}_4\text{H}_3\text{S-3})_2$ ,  $m$ . 86°.<sup>24, 25</sup>  
 $\text{Me}(\text{C}_4\text{H}_3\text{O-2})\text{C}(\text{SEt})_2$ ,  $b_{2.5}$  93–6°.<sup>88a</sup>  
 $\text{CH}_2(\text{CH}_2\text{CH}_2)_2\text{C}(\text{SMe})_2\text{C}(\text{SMe})_2$ ,  $b_{1.4}$  73–5°;  $d_{25}$  1.0504;  $n$  25/D 1.5384.<sup>31.5</sup>  
 $\text{CH}_2(\text{CH}_2\text{CH}_2)_2\text{C}(\text{SEt})_2$ ,  $b_{12}$  67–110°.<sup>129a</sup>  
 $\text{CH}_2(\text{CH}_2\text{CH}_2)_2\text{C}(\text{SCH}_2\text{Ph})_2$ ,  $b_{0.05}$  165–7°,<sup>69</sup>  $b_{0.15}$  196°;  $n$  25/D 1.6050.<sup>162.5</sup>  
 $(\text{EtSCH}_2)_2\text{C}(\text{SEt})_2$ ,  $b_{15}$  51–3°.<sup>137</sup>
- $\text{Me}_2\text{C}(\text{SeEt})_2$ ,  $b_4$  81°;  $d$  0/4 1.4574,  $d$  25/4 1.4288.<sup>157</sup>  
 $\text{MeEtC}(\text{SeEt})_2$ ,  $b_{3.5}$  91.5°;  $d$  0/4 1.4291,  $d$  25/4 1.4023.<sup>157</sup>  
 $\text{Et}_2\text{C}(\text{SeEt})_2$ ,  $b_{3.5}$  104.5°;  $d$  0/4 1.3823,  $d$  25/4 1.3568.<sup>157</sup>  
 $\text{Ph}_2\text{C}(\text{SBu-}t)_2$ ,  $m$ . 84°.<sup>162</sup>  
 $\text{Ph}_2\text{C}(\text{SPh})_2$ ,  $m$ . 137°,<sup>154</sup> 223°.<sup>15</sup>  
 $\text{Ph}_2\text{C}(\text{SCH}_2\text{Ph})_2$ ,  $m$ . 252°.<sup>15</sup>  
 $\text{Ph}_2\text{C}(\text{SC}_6\text{H}_4\text{Me-}p)_2$ ,  $m$ . 73°.<sup>152</sup>  
 $\text{Ph}_2\text{C}(\text{SC}_{10}\text{H}_7)_2$ ,  $\beta$ ,  $m$ . 133°.<sup>152</sup>  
 $\text{Ph}_2\text{C}(\text{SC}_4\text{H}_3\text{S-3})_2$ ,  $m$ . 152°.<sup>24, 25</sup>  
 $\text{Ph}_2\text{C}(\text{SC}_4\text{H}_3\text{O-2})_2$ ,  $m$ . 152°.<sup>24</sup>  
 $\text{Ph}(\text{C}_{10}\text{H}_7)\text{C}(\text{SCH}_2\text{Ph})_2$ ,  $\alpha$ -  $m$ . 136°;  $\beta$ -  $m$ . 98°.<sup>150</sup>  
 $(\text{PhCH}_2)_2\text{C}(\text{SCH}_2\text{Ph})_2$ ,  $m$ . 103°.<sup>149</sup>  
 $(p\text{-PhC}_6\text{H}_4)\text{PhC}(\text{SCH}_2\text{Ph})_2$ ,  $m$ . 108°.<sup>150</sup>

$(p\text{-PhC}_6\text{H}_4)\text{C}(\text{SCH}_2\text{Ph})_2$ , m.  $116^\circ$ .<sup>150</sup>  
 $(p\text{-ClC}_6\text{H}_4)\text{PhC}(\text{SCH}_2\text{Ph})_2$ , m.  $107^\circ$ .<sup>150</sup>  
 $(p\text{-ClC}_6\text{H}_4)_2\text{C}(\text{SCH}_2\text{Ph})_2$ , m.  $95^\circ$ .<sup>150</sup>  
 $(p\text{-NO}_2\text{C}_6\text{H}_4)\text{PhC}(\text{SCH}_2\text{Ph})_2$ , m.  $105^\circ$ .<sup>150</sup>  
 $[2,4\text{-(HO)}_2\text{C}_6\text{H}_3]\text{PhC}(\text{SBu})_2$ , m.  $250^\circ$ .<sup>15</sup>  
 $[3,4\text{-Me(MeO)C}_6\text{H}_3]_2\text{C}(\text{SCH}_2\text{Ph})_2$ , m.  $93^\circ$ .<sup>150</sup>  
 $(p\text{-MeSC}_6\text{H}_4)_2\text{C}(\text{SPh})_2$ , m.  $119^\circ$ .<sup>113</sup>  
 $(o\text{-MeOC}_6\text{H}_4)_2\text{C}(\text{SCH}_2\text{Ph})_2$ , m.  $108^\circ$ .<sup>150</sup>  
 $\text{MeC}(\text{SPh})_2\text{C}(\text{SPh})_2\text{Me}$ , m.  $165^\circ$ .<sup>122a</sup>  
 $\text{MeCOCH}_2\text{C}(\text{SEt})_2\text{Me}$ ,  $b_{215}$   $179\text{--}83^\circ$ ,  $b_{240}$   $180\text{--}5^\circ$ ; d  $13.5/4$   $2.007$ .<sup>99</sup>  
 $\text{PhCOCH}_2\text{C}(\text{SEt})_2\text{Ph}$ , m.  $60^\circ$ .<sup>121c</sup>  
 $\text{MeC}(\text{SR})_2\text{CH}_2\text{CH}_2\text{C}(\text{SR})_2\text{Me}$ , R=Me, m.  $75^\circ$ .<sup>133</sup>  
 Et, m.  $27^\circ$ ; d  $25/4$   $1.036$ ; n  $25/D$   $1.5390$ .<sup>133</sup>  
 Pr, m.  $-9.5^\circ$ ; d  $25/4$   $1.000$ , n  $25/D$   $1.5260$ .<sup>133</sup>  
 Bu, m.  $-9.0^\circ$ ; d  $25/4$   $0.978$ ; n  $25/D$   $1.5151$ .<sup>133</sup>  
 Am, m.  $-6.5^\circ$ ; d  $25/4$   $0.9572$ ; n  $25/D$   $1.5098$ .<sup>134</sup>  
 Hex, m.  $11.5^\circ$ ; d  $25/4$   $0.946$ ; n  $25/D$   $1.5060$ .<sup>133</sup>  
 Hept, m.  $31^\circ$ .<sup>134</sup> Oct, m.  $38^\circ$ .<sup>133</sup> Non, m.  $50^\circ$ .<sup>134</sup> Dec, m.  $58^\circ$ .<sup>133</sup>  
 Undec, m.  $61^\circ$ .<sup>134</sup> Dodec, m.  $66^\circ$ .<sup>133</sup> Tetradec, m.  $73^\circ$ .<sup>30</sup> Octa-  
 dec, m.  $82^\circ$ .<sup>30</sup> Ph, m.  $138^\circ$ .<sup>122a</sup>  $\text{PhCH}_2$ , m.  $99^\circ$ .<sup>122a</sup>

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# Mercaptals and Mercaptoles of the Sugar Group

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Mercaptal formation has been of great service to researchers in the sugar group for the isolation and identification of aldoses. Thus, glucose is soluble in 3 parts of water at 0° and in 1.25 parts at 25° while its ethyl mercaptal is only slightly soluble and separates in long needles which have a sharp melting point and characteristic rotation. Converting an aldose into a mercaptal and then demercaptalating it back to the same aldose<sup>38b, 41</sup> has been used for obtaining sugars which can be isolated in no other way. In a mercaptal the aldose is fixed in the open chain, aldehyde form. After derivatives of this have been made the mercaptan can be removed leaving a derivative of the aldehyde form.

The chemistry of the sugar group is so intricate that far more space than is here available would be required to go into the details of the formation and properties of the individual mercaptals of the many sugars. A number of references are given so that particular mercaptals can be traced. The subject has been reviewed.<sup>51</sup>

### Formation

The story begins with Emil Fischer in 1894. He made mercaptals from ethyl mercaptan with glucose, galactose, mannose,



arabinose, rhamnose, and  $\alpha$ -glucoheptose but did not get them from fructose and sorbose. Lactose and sorbose reacted but the mercaptals did not crystallize out. His method, with slight variations, is still standard. To a mixture of 70 g. of glucose and 70 g. hydrochloric acid, cooled in ice, 40 g. of ethyl mercaptan were added in four portions with vigorous shaking. The mercaptal separated out in 10 to 20 minutes and was recrystallized from alcohol. It melted at 128°. Hydrobromic, 50% sulfuric acid, and 50% zinc chloride solution were satisfactory as catalysts.<sup>14</sup>

Mercaptals have been used extensively for the identification of sugars.<sup>52, 69, 71, 73b, 82</sup> For example, 1 g. of the aldose, 1 cc. of concentrated hydrochloric acid and 1 cc. of methyl mercaptan are shaken together, cooled to 0°, and 2 cc. of water added.<sup>95b</sup> Other mercaptans may be used. A single mercaptal gives a double identification since both its melting point and rotation are characteristic and may be compared with those of known sugars.

Sugars, which resist isolation by other means, have been gotten out as mercaptals.<sup>15, 61</sup>

The rate of the hydrolysis of starch has been measured by determining the amount of mercaptal formation in samples taken at intervals of time.<sup>84</sup> A starch hydrolyzate has been treated with a mercaptan and the average size of the molecules estimated from the sulfur content. In one experiment at the end of 20.5 hours the average molecule contained only 3 glucose units.<sup>77, 78</sup> The hydrolysis of cellulose<sup>72</sup> and of methyl cellulose was followed similarly.<sup>72, 85</sup> The hydrolysis of sucrose has been followed with butyl mercaptan.<sup>59</sup>

Optically active amyl mercaptan has been used for resolving racemic aldoses.<sup>65</sup> The changes of rotation due to mercaptalation have been studied.<sup>2</sup>

Of all the mercaptans the ethyl has been the one most commonly employed for preparing mercaptals. It has been used with glucose,<sup>5, 6, 7, 14, 15, 24, 28, 29, 30b, 38b, 46, 47, 55, 57, 60, 68, 72, 73a, 83, 86, 91, 93, 95b</sup> galactose,<sup>14, 18, 30b, 39, 40, 66, 67, 68, 70, 73a, 83, 87, 93, 95b</sup> arabinose,<sup>2, 13, 14, 18, 30b, 70, 94, 95b</sup> mannose,<sup>14, 17, 28, 42, 49, 53, 60, 70, 75, 95b</sup> rhamnose,<sup>14, 18, 95b</sup> isorhamnose,<sup>16</sup> maltose,<sup>74, 80</sup> lyxose,<sup>76</sup> xylose,<sup>11, 80, 83</sup> fucose,<sup>65, 81</sup>  $\alpha$ -glucoheptose,<sup>14</sup> 2-methylglucose,<sup>30b</sup> tetracetylglucose,<sup>91</sup> pentaacetylglucose,<sup>56, 88, 89</sup> tetrabenzoylglucose,<sup>8, 9a, 9b</sup>

pentabenzoylglucose,<sup>9b</sup>  $\alpha$ -galaheptose,<sup>19</sup> 5-ketorhamnose,<sup>64</sup> iodo-diacetone-galactose,<sup>35</sup> tetraacetylfucose,<sup>81</sup> rhodose,<sup>65</sup>  $\alpha$ -manno-heptose,<sup>36</sup> galagalactose,<sup>20</sup> arabomethylose,<sup>52, 61</sup> acetone-arabomethylose,<sup>27</sup> pentaacetylgalactose,<sup>10b, 49, 88, 92</sup> the lactone of 5-ketorhamnose,<sup>64</sup> and galactouronic acid.<sup>10a, 12</sup> The crystal form of glucose diethylmercaptan has been determined.<sup>24</sup> Its conductivity in boric acid solution has been measured in a study of its configuration.<sup>32.5</sup>

Methyl mercaptals have been made from glucose,<sup>56, 57, 95b</sup> galactose,<sup>95b</sup> arabinose,<sup>70, 95b</sup> mannose,<sup>95b</sup> ribose,<sup>22, 95a</sup> rhamnose,<sup>95b</sup> lyxose,<sup>22</sup> and 5-ketorhamnose and its lactone.<sup>64</sup>

Propyl mercaptan has been used with glucose,<sup>33, 50, 56, 57</sup> galactose,<sup>33, 50</sup> arabinose, mannose,<sup>33</sup> ribose,<sup>95a</sup> maltose, rhamnose,<sup>33</sup> and 5-ketorhamnose and its lactone<sup>64</sup> and *i*-propyl with glucose, galactose, mannose, arabinose, rhamnose,<sup>95b</sup> and ribose.<sup>95a, 95b</sup> Mercaptals have been made from butyl mercaptan and glucose, galactose,<sup>50, 63</sup> arabinose, mannose, rhamnose, maltose, lactose,<sup>63</sup> and ketorhamnose,<sup>64</sup> from *i*-butyl mercaptan and glucose, galactose, arabinose, mannose, rhamnose,<sup>62, 95b</sup> maltose,<sup>62</sup> and ribose<sup>95a, 95b</sup> and from *i*-amyl mercaptan and arabinose<sup>37</sup> and glucose.<sup>14</sup> *D*-Amyl and *i*-amyl mercaptans have been used with arabinose, rhodose, fucose, glucose, and galactose.<sup>65</sup> Glucose, galactose, arabinose, mannose, and xylose have been made to react with hexyl mercaptan<sup>22.5</sup> and glucose and galactose with heptyl mercaptan.<sup>50</sup>

Mercaptals have been made from benzyl mercaptan with glucose,<sup>22, 25, 30b, 38a, 43, 48</sup> arabinose,<sup>1.5, 25, 43</sup> galactose,<sup>22, 25, 32, 43, 44a, 45</sup> rhamnose,<sup>25, 43</sup> xylose,<sup>29, 30b</sup> lyxose,<sup>22</sup> mannose,<sup>44b</sup> fucose,<sup>54</sup> ribose,<sup>22, 95a</sup> and *D*-gluco- $\alpha$ -*L*-galactose.<sup>21</sup> Cysteine forms mercaptals with glucose, lactose, galactose, arabinose, mannose, and xylose.<sup>58</sup> Glucose mercaptals have been made with oleyl<sup>26</sup> and thenyl<sup>23</sup> mercaptans. Ethylene mercaptan has been used with glucose, galactose, mannose, rhamnose,<sup>25</sup> lyxose,<sup>22</sup> ribose,<sup>22, 95a</sup> rhodose, fucose,<sup>65</sup> and arabinose<sup>25</sup> and trimethylenedimercaptan with glucose and arabinose.<sup>25</sup>

A glucofuranose reacts with three molecules of mercaptan. The abstraction of two of these by mercuric chloride leaves 2-ethylthiogluucose.<sup>9b</sup> The lactone of 5-ketorhamnose is converted to 4-ethylmercapto-5-methylfuroic acid.<sup>64</sup> In the absence of a cata-

lyst, tetrabenzoylglucose and ethanethiol give the hemimercaptal.<sup>8</sup> D-Galacturonic acid gives a mercaptal under the usual conditions.<sup>10a</sup> If methanol is present there is simultaneous esterification.<sup>12</sup>

Compared with the mercaptals of the aldoses the known mercaptoles of the ketoses are few in number. In general ketones are considerably less reactive than aldehydes. Aldoses, as well as ketoses, are unstable in the presence of strong acids. With some ketoses the destruction by the acid may outrun the reaction with the mercaptans. Some of the products may be too soluble to isolate. Mercaptoles have been prepared from fructose<sup>9c, 38d, 88</sup> and from pentaacetylfructose.<sup>88</sup> A synthesis recently discovered by Wolfrom through the keto-acetates makes possible the preparation of any desired mercaptole.<sup>90</sup>

### Reactions

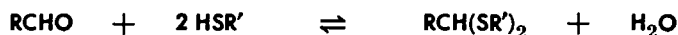
These belong to two classes, those that affect the mercaptal portion and those that have to do with the rest of the molecule. Mercaptalation does not affect the reactivity of the hydroxyl groups of a sugar. Converting a cyclic aldose to the open chain form of a mercaptal provides an additional hydroxyl.

By the usual methods mercaptals may be acetylated,<sup>1, 5, 6, 10a, 12, 19, 20, 22, 32, 34, 35, 36, 42, 49, 53, 54, 56, 66, 68, 70, 73b, 76, 79, 80, 81, 83, 91, 94</sup> benzoylated,<sup>1, 1.5, 4b, 5, 6, 7, 9c, 29, 30b, 70, 72, 82, 83</sup> tritylated,<sup>1, 34, 70, 83, 91</sup> or methylated.<sup>11, 30a, 38b, 41, 44b, 54</sup> The acetyl, benzoyl, and trityl groups can be removed by conventional means. The presence of the mercaptal group does not affect the reactivity of a sugar toward acetone<sup>1.5, 5, 11, 38a, 38c, 40, 41, 44a, 54, 60</sup> or benzaldehyde.<sup>87, 91</sup> Benzaldehyde may replace the mercaptan. Thus 6-benzoyl glucose mercaptal is converted to 6-benzoyldibenzylideneglucose.<sup>47, 86</sup>

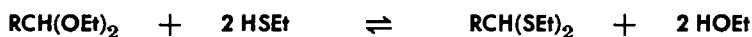
A mercaptal dissolves in aqueous alkali from which it may be precipitated by acid unchanged.<sup>50</sup> Glucose diethylmercaptal,<sup>29</sup> or its benzoyl derivative,<sup>9a</sup> may be methylated in the 2-position by shaking with silver oxide and methyl iodide. Sodium ethylate may be used instead of the silver oxide.<sup>47</sup> The mannose mercaptal can be methylated up to the pentamethyl derivative by methyl sulfate.<sup>28</sup> The diethyl mercaptal of glucose is converted into the pentacarbanilo derivative by treatment with phenylisocyanate.<sup>67</sup>

### Demercaptalation

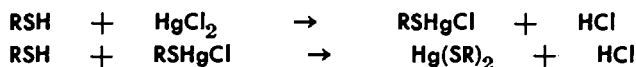
Earlier in chapter 5 it was shown that the formation of a mercaptal is a reversible reaction:



Normally the equilibrium is far to the right. However, if the free mercaptan is eliminated, the equilibrium will be shifted to the left. The equilibrium between alcohols and mercaptans and the corresponding acetals and mercaptals has been mentioned:



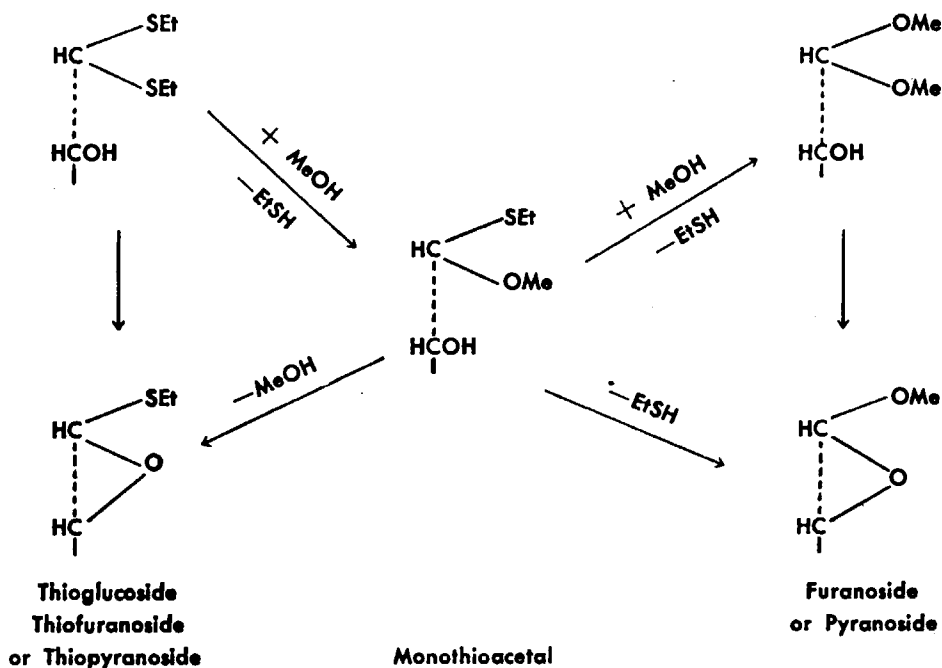
Aldose mercaptals are hydrolyzed by boiling with dilute acids.<sup>14, 50</sup> This is due to the large excess of water and to the volatility of the mercaptan. The elimination of the mercaptan in this way is slow. Demercaptalation goes to completion rapidly if there is something present which reacts rapidly and completely with the mercaptan as it is liberated. Silver nitrate, mercuric chloride and cadmium chloride remove the mercaptan as insoluble mercaptides.<sup>14</sup> The reaction of mercuric chloride with the mercaptan liberates hydrochloric acid:



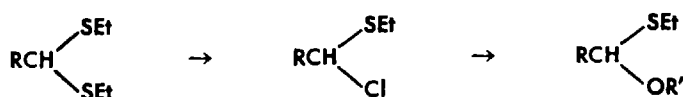
Keeping the acidity down favors the formation of the less soluble mercaptide  $\text{Hg}(\text{SR})_2$ . This may be done by mercuric oxide<sup>10b, 11, 38d, 39</sup> or cadmium carbonate.<sup>1, 13, 19, 20, 34, 68, 70, 75, 79, 81, 89</sup> The cadmium ion is said to act as a catalyst.<sup>88</sup> Demercaptalation has been shown to take place in the body of a dog.<sup>48</sup>

A mechanism has been worked out that accounts for the various products which are formed when an aldose mercaptal is treated with mercuric chloride, in solution in an alcohol.<sup>38d</sup> The mercaptan which is eliminated at each step is taken care of by the mercuric chloride. The assumed intermediates,  $-\text{CH}(\text{SEt})\text{Cl}$  and  $-\text{CH}(\text{OMe})\text{Cl}$ , are left out. If an alcohol is present the ethylmercapto group may be replaced by an alkoxy. The aldose is a poly-alcohol and in the absence, or even in the presence, of an alcohol a reaction may occur which will involve the most suitably placed hydroxyl. An alkoxy group may be replaced as well as an alkylmercapto. Some of the reactions are represented in the diagram. Just which one will predominate de-

depends on the proportions of the reactants and on the conditions. The desulfurization is limited by the amount of mercuric chloride present.



When an aldose mercaptal is treated with a mixture of acetyl chloride and phosphorus oxychloride one of the alkylmercapto groups is replaced by chlorine. The reaction of an alcohol with this gives the monothioacetal: <sup>92</sup>



Acetyl bromide reacts similarly. <sup>93</sup> A monothioacetal is represented as the key intermediate in the diagram above. Monothioacetals from the demercaptalation of mercaptals <sup>75, 93</sup> and of fructose mercaptol <sup>38d, 88</sup> have been reported.

When no alcohol is added one of the hydroxyl groups of the sugar serves instead. This is the replacement of a volatile mercaptan by a non-volatile alcohol. Thus, when glucose mercaptal is boiled with 22% aqueous hydrochloric acid,  $\alpha$ -ethylthioglucopyranoside is formed. <sup>5, 46</sup> A low yield of the same compound may be obtained from glucose with only one equivalent of mercaptan in the presence of hydrochloric acid. <sup>46</sup> A number of thioglucosides

have been made by the demercaptalation of mercaptals.<sup>5, 38d, 46, 55, 91</sup> Tetraacetylthio- $\beta$ -D-mannopyranoside has been made in this way.<sup>17</sup> This reaction has been studied with reference to the Walden inversion.<sup>57</sup> The rate of hydrolysis of  $\alpha$ -ethylthioglucofuranoside has been measured and a mechanism suggested.<sup>46</sup>

Dimethylacetals have been prepared of mannose,<sup>42, 48, 53</sup> galactose,<sup>10b, 87</sup> 4,5-acetonegalactose,<sup>45</sup> pentaacetylgalactose,<sup>10b</sup> and glucose<sup>89</sup> by demercaptalating their mercaptals in methanol. The glucose dimethylacetal had been long sought.<sup>4a</sup> Mannose dimethylacetal<sup>42, 53</sup> and a fructose ketole have been made similarly.<sup>38d</sup>

The mercapto groups of a mercaptal may be replaced by two —OAc by treatment with acethanhydride in the presence of sulfuric acid or of pyridine. Thus heptaacetates of glucose, mannose, and galactose<sup>49</sup> and hexaacetates of lyxose,<sup>76</sup> arabinose, and xylose have been prepared.<sup>49</sup>

$\alpha$ -Alkylpyranosides are prepared by boiling sugar mercaptals with alcohols in the presence of mercuric chloride.<sup>18</sup> Glucose,<sup>38b</sup> arabinose, galactose, and rhamnose pyranosides have been prepared in this way.<sup>43</sup>

If, however, this reaction is effected at a low temperature and the hydrochloric acid neutralized as it is liberated, as by yellow mercuric oxide, the products are furanosides.<sup>39</sup> This is an important general method for the preparation of furanosides which are otherwise difficult to prepare. Furanosides of glucose,<sup>18, 46, 93</sup> galactose,<sup>18</sup> mannose,<sup>42, 44b, 53</sup> rhamnose,<sup>18</sup> arabinose,<sup>61</sup> and even of fructose<sup>38d</sup> have been made in this way.

The demercaptalation of mercaptals has been used in preparing a host of sugar derivatives of which only a few examples can be given here. As is well known an aldose exists in either the one or the other of two cyclic forms in equilibrium with a very small amount of the open chain aldehyde. Thus there are normally only four hydroxyls of a hexose that can be acetylated or benzoylated. As mercaptal formation fixes the glucose in the aldehyde form there are five open hydroxyls.

The mercaptal of glyceraldehyde is acetylated and then demercaptalated to give the aldehydo-diacetate,  $\text{AcOCH}_2\text{CH}(\text{OAc})\text{-CHO}$ .<sup>1</sup> The diisopropylidene derivative of arabinose mercaptal was converted to the diisopropylidene derivative of aldehydo-arabinose.<sup>13</sup> The corresponding tetraacetate was obtained simi-

larly.<sup>79</sup> The same can be said of aldehydo-fucose tetraacetate.<sup>81</sup> Glucose pentaacetate<sup>56, 68</sup> and pentabenzoate<sup>7, 70</sup> have been prepared through the mercaptal. The pentaacetates of galactose<sup>68</sup> and mannose<sup>75</sup> have been obtained similarly. The pentamethyl derivatives of mannose and glucose have been made by demercaptalating the methylated mercaptals.<sup>28</sup> The acetylated mercaptals were used in the preparation of  $\alpha$ -galaheptose<sup>19</sup> and  $\alpha$ -manoheptose<sup>36</sup> hexaacetates. The heptaacetate of D-gala-L-galaotose<sup>20</sup> and the octaacetate of aldehydo-maltose<sup>74</sup> have been obtained through the mercaptals. In some cases the carbon chain is broken.<sup>1.5, 88.5</sup>

Desoxy compounds are obtained from the mercaptals of glucose, galactose, and fructose by treatment with Raney nickel.<sup>4b, 73a</sup> It has been proposed to reduce the undesirable odor of hydrocarbon distillates by treating them with glucose and acid to form mercaptals.<sup>3</sup> Acetylated mercaptals are oxidised to the disulfones by a peracid. This may be used for the degradation of a sugar.<sup>81</sup>

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## CHAPTER 7.

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# Disulfides and Polysulfides

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### Disulfides



Alkyl disulfides correspond to alkyl peroxides,  $\text{RO}\cdot\text{OR}$ . The formulac of the two classes look alike but here the similarity ends. The disulfides are easily prepared and perfectly stable while the peroxides are unstable, some of them dangerously explosive.

### OCCURRENCE

The most remarkable occurrence of a disulfide, so far reported, is methyl disulfide in cavities in quartz of the paleozoic period.<sup>740</sup> Methyl disulfide and isopropyl disulfide are in the odor from eucalyptus.<sup>653</sup> Methyl disulfide is present in the gases from sulfite pulp digesters.<sup>233, 311</sup> Allyl disulfide<sup>10, 133, 134, 728, 774, 838</sup> and allyl propyl disulfide<sup>466b, 466c, 728</sup> are found in oil of garlic and allyl *s*-butyl disulfide in asafetida.<sup>514</sup> Allicin appears to be the monosulfoxide of allyl disulfide,  $\text{H}_2\text{C}:\text{CHCH}_2\text{SO}\cdot\text{SCH}_2\text{-CH}:\text{CH}_2$ . This is a thioester of a sulfinic acid. With cysteine it gives the disulfide  $\text{H}_2\text{C}:\text{CHCH}_2\text{SSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ .<sup>135</sup> A butyl disulfide is present in the secretion of the skunk.<sup>54, 237</sup> The essential oil of *Agathosma apiculata* Meyer contains 30% of butyl 1-pentenyl disulfide.<sup>747</sup>

Cystine,  $(\text{-SCH}_2\text{CHNH}_2\text{CO}_2\text{H})_2$ , so important in proteins is a disulfide acid, and so is the recently discovered  $\alpha$ -lipoic acid. A number of hormones and enzymes have been shown to have, or are suspected of having, disulfide linkages. Oxytosin, glutelin, pantothenic acid, and insulin may be mentioned.

Disulfides are found in crude benzene<sup>581</sup> and in petroleum distillates<sup>204, 420, 860</sup> but they are supposed to have been formed by the oxidation of mercaptans.<sup>234</sup>

### HISTORY

The history of disulfides is coextensive with that of mercaptans and monosulfides. It was natural for Zeise, and those who followed him, after they had obtained mercaptans by heating potassium hydrosulfide with alkyl sulfates, to try their luck with potassium disulfide and with "liver of sulfur," a polysulfide. They got alkyl disulfides and polysulfides, which broke down into disulfides and sulfur on distillation. Some disulfides were made from the mercaptans by oxidation. In 1834 Zeise distilled ethyl disulfide out of a mixture of potassium ethyl sulfate and barium disulfide.<sup>865</sup> Morin in 1839,<sup>551</sup> Cahours in 1846,<sup>128</sup> and Muspratt in 1851<sup>566</sup> got the same product though they used metal pentasulfide and tri-sulfides. Cahours prepared methyl disulfide also.<sup>128</sup> *i*-Amyl disulfide was made similarly from potassium disulfide by Henry in 1840<sup>362</sup> and by Danson in 1851.<sup>178</sup>

### FORMATION

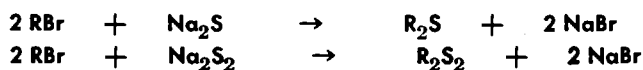
#### *Oxidation of Mercaptans*

The neatest way to get a pure alkyl or aryl disulfide is by the oxidation of the corresponding mercaptan. This has been discussed in chapter 2, Volume I, on mercaptan reactions so is only mentioned here.

Pentachlorothiophenol is converted to the disulfide by phosphorus pentachloride.<sup>788.5</sup>

#### *From Metal Disulfides*

Since an alkyl halide and sodium sulfide give the alkyl sulfide it is natural to expect an alkyl disulfide from sodium disulfide:



In fact, alkyl disulfides are obtained by this reaction in fair yields. The catch is that sodium disulfide is a statistical compound, that is, it is a mixture of  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{S}_2$ ,  $\text{Na}_2\text{S}_4$ , and possibly  $\text{Na}_2\text{S}_5$  and  $\text{Na}_2\text{S}_6$ . In a recorded experiment, ethyl bromide and potassium disulfide gave a mixture of ethyl sulfide, disulfide, trisulfide, and higher polysulfides.<sup>380b</sup> With the lower alkyl disulfides this is not serious since they can be separated from the mono- and poly-sulfides by fractionation. The wide differences in the boiling points make this easy. The polysulfides are left in the residue. The boiling points for several pairs are given in Table 1.7.

TABLE 1.7

*Boiling Points of Some Sulfides and Disulfides*

	Methyl	Ethyl	Propyl	Butyl
Sulfide	37.3°	92.2°	142°	182°
Disulfide	109.75°	152°	193°	230°
Difference	72.4°	60°	51°	48°

As was mentioned above, sodium or potassium alkyl sulfates were the alkylating agents in early times. They are still employed occasionally.<sup>179, 194, 433</sup> They have the advantage that they are soluble in water which is the best solvent for sodium disulfide. Alkyl halides have largely supplanted them.<sup>85a, 222, 276, 536, 548, 582, 605, 649, 739, 748, 800</sup> They are commonly used with alcohol, or dilute alcohol, solutions of sodium disulfide but may be used with an aqueous solution.<sup>851</sup> Disulfides in the sugar group have been made from the corresponding bromides.<sup>856, 857</sup> A halogen attached to an aromatic ring must be activated, as by a properly placed nitro group.<sup>85f, 92a, 95c, 218, 270, 273, 279, 372, 374, 375, 416, 521, 547, 627b, 672, 790</sup> Chlorobenzene does react with calcium sulfide at 300° but the product is a mixture.<sup>501</sup> Aromatic disulfides can be prepared from diazonium chlorides and metal disulfides.<sup>39, 318, 677</sup> Sometimes a disulfide is obtained instead of an expected mercaptan.<sup>61, 126</sup> This may be due to fortuitous oxidation. Chloromethyl ether,  $\text{MeOCH}_2\text{Cl}$ , which is sensitive to water or alcohol, has been made to react with solid potassium disulfide.<sup>462</sup> There are several ways to obtain alkyl disulfides from alkyl thiosul-

fates.<sup>83, 274, 455, 626, 635, 757, 782, 805, 812b, 815, 841</sup> Alkaline hydrolysis is one of these. The same treatment converts alkyl or aryl thiocyanates to disulfides.<sup>293b, 379</sup>

### *From the Action of Sulfur on Organic Compounds*

Disulfides are formed when various organic compounds are heated with sulfur. The results are seldom clean cut. Monosulfides, trisulfides, and other products are commonly formed, the proportions of these depending on the nature of the starting compounds and on the conditions of heating. Disulfides have been obtained from phenols,<sup>337, 470a</sup> naphthols,<sup>593</sup> aniline,<sup>470a</sup> saturated<sup>533, 798</sup> and unsaturated<sup>13, 18, 19, 574, 727b, 827, 837</sup> hydrocarbons, benzene,<sup>312</sup> squalene,<sup>87</sup> and tin tetraphenyl<sup>100</sup> by heating them with sulfur. Trifluoromethyl<sup>108, 350.5</sup> and perfluoropropyl<sup>353</sup> iodides, when heated with sulfur, give mixtures of disulfides and trisulfides while iodine is given off. Certain aldehydes and ketones give good yields of disulfides when heated with hydrogen sulfide.<sup>129</sup> When a mixture of 1-methylcyclohexene and sulfur, with some acetone, is irradiated a disulfide is among the products.<sup>575</sup> An unsaturated disulfide is formed from amylene and sulfur under certain conditions.<sup>118</sup> Ammonium sulfide converts cyclohexanone into cyclohexyl disulfide<sup>864</sup> and acetophenone into  $\alpha$ -methylbenzyl disulfide.<sup>51</sup> Diphenylmethyl disulfide can be obtained from benzophenone in several ways.<sup>1, 760a</sup> A 70% yield of this disulfide is formed when diphenylmethylen chloride,  $\text{Ph}_2\text{CCl}_2$ , is treated with sodium hydrosulfide.<sup>761</sup>

### *From the Action of Sulfur Chlorides on Organic Compounds*

Acetylacetone,<sup>11, 507, 507.5, 816</sup> isobutyraldehyde,<sup>580</sup> thiophene,<sup>442</sup> acetoacetanilides,<sup>438.5, 568.2</sup> malonamides,<sup>568, 568.4</sup> cyanoacetamides<sup>568.6</sup> and aromatic hydrocarbons<sup>428.5, 738c</sup> give disulfides when they are treated with sulfur monochloride. This acts as a chlorinating as well as a sulfurizing agent with trithioformaldehyde producing  $(\text{ClCH}_2)_2\text{S}_2$ .<sup>180</sup> Phenols, naphthols,<sup>6, 303, 360</sup> and dimethylaniline<sup>467</sup> are converted to mixtures of disulfides and polysulfides as is described in chapter 1, Volume II. Some disulfide is formed along with the monosulfide and polysulfides, by the reaction of sulfur chloride with ethylene,<sup>429, 611</sup> perfluoroethylene,<sup>637</sup> amylene,<sup>615</sup> and other unsaturates.<sup>533</sup> The addition



of *o*-nitrophenyl dithiochloride,  $o\text{-O}_2\text{NC}_6\text{H}_4\text{SSCl}$ , to an unsaturated gives a disulfide.<sup>347</sup>

### Miscellaneous Methods

A Grignard reagent is converted by an excess of sulfur,<sup>389, 787a, 858c, 859</sup> by sulfur monochloride,<sup>778b</sup> or by sulfur dichloride<sup>235</sup> to a disulfide.

An alkyl<sup>90</sup> or aryl<sup>451</sup> sulfide may be sulfurized to a disulfide but this is a slow reaction even at  $180^\circ$ .<sup>90, 451</sup> *p*-Nitrophenyl sulfide, in which the para nitro group has a labilizing influence, is readily sulfurized.<sup>284</sup>

Disulfides may be formed in the course of the reduction of sulfonyl chlorides<sup>50, 143, 157, 215, 243, 252, 303, 577, 696a, 767</sup> or bromides.<sup>434</sup> A 57% yield of the disulfide has been obtained by treating benzenesulfonic anhydride with hydrogen bromide<sup>244.5</sup> but the same treatment converted methanesulfonic anhydride to the sulfonyl bromide.<sup>245.5</sup> Sodium *m*-nitro-*p*-toluenesulfonate has been reduced electrolytically to the aminotolyl disulfide.<sup>240</sup> When a sodium aryl sulfonate is treated with phosphorus tribromide more or less of the aryl disulfide is formed. This may be the major product.<sup>394, 443</sup> Sulfinic acids may be reduced to disulfides.<sup>267, 268</sup> Disulfides appear to be intermediates in the lithium aluminum hydride reduction of aryl sulfonylchlorides, sulfinic acids, and the like to mercaptans.<sup>777</sup> Under proper conditions the disulfides can be isolated.<sup>245</sup> Disulfides may be obtained by hydrolyzing thiosulfonic esters,  $\text{RSO}_2\cdot\text{SR}'$ ,<sup>309, 598a, 598b, 608</sup> or by treating them with phosphorus trichloride.<sup>438</sup> When a sodium sulfinate,  $\text{C}_6\text{H}_{11}\text{SO}_2\text{Na}$  or  $\text{C}_5\text{H}_9\text{SO}_2\text{Na}$ , is refluxed with *t*-butyl bromide, the disulfide is formed. The hydrobromic acid, which is split off, sets free the sulfinic acid which disproportionates.<sup>812a</sup>

Mercury converts a sulfonyl chloride to a disulfide:<sup>113.3, 114.5</sup>



An unexpected by-product of the alkylation of an aryl mercaptan by an alkyl sulfate, in the absence of alkali, is the disulfide.<sup>63</sup> A half-way product,  $[o\text{-(EtO)}_2\text{CHCH}_2\text{SC}_6\text{H}_4\text{S}]_2$ , is formed from *o*-dimercaptobenzene.<sup>602</sup>

The chlorination products of propylene<sup>769</sup> and trimethylene<sup>768</sup> sulfides are, respectively,  $(\text{ClCH}_2\text{CHMe})_2\text{S}_2$  and  $(\text{ClCH}_2\text{CH}_2\text{-CH}_2)_2\text{S}_2$ .

2-Thienyl disulfide is a by-product in the preparation of thiophene from succinic acid and phosphorus pentasulfide.<sup>534</sup>

Disulfides are among the products when certain organic compounds are subjected to hydrogen sulfide under 8500 atmospheres pressure at 125–150°. <sup>130</sup>

Many of these are not presented as preparation methods but as examples of the various ways in which disulfides can be formed.

### *Unsymmetrical Disulfides*

Treating a mixture of two mercaptans with bromine gives a mixture of three disulfides, one of which is unsymmetrical.<sup>598c</sup> Any other oxidising agent does the same.<sup>500</sup> These disulfides may be separated by fractionation.

An unsymmetrical disulfide may be obtained from two symmetrical by redistribution:

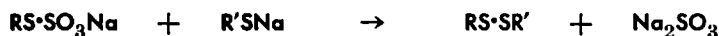


As this reaction is reversible the product will be an equilibrium mixture. This is catalyzed by a trace of mercaptan which is almost sure to be present. The reduction of disulfides by mercaptans is discussed later. Methyl ethyl disulfide disproportionates: <sup>79</sup>

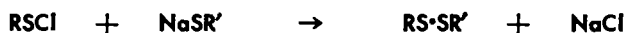


Naturally the reaction will go to completion if one of the products is removed. Redistribution in the presence of sodium hydrosulfide or of a sodium mercaptide will be taken up later. The interchange of cystine with penicillamine disulfide,<sup>786.5</sup> with 2,4-dinitrophenyl cystine,<sup>690.7</sup> and with dithiodiglycolic acid<sup>685</sup> has been studied. The changes in gelation times of proteins under various treatments has been attributed to the breaking and reformation of the cystine disulfide bonds.<sup>261.5, 338.5, 388.4, 388.6, 393.5</sup> The reduction in viscosity of thioelastomers when treated with alkyl disulfides is evidence of redistribution.<sup>70.5</sup>

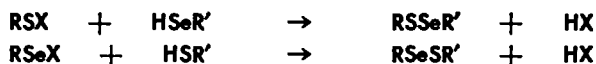
The reaction of a mercaptide with a Bunte salt gives a mixed disulfide: <sup>250</sup>



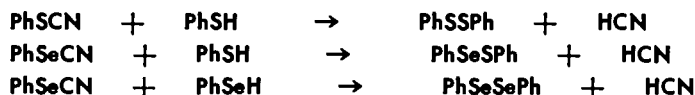
The neat way to get a pure unsymmetrical disulfide is by the reaction of a sulfenyl halide on a mercaptide: 113.7, 114.5, 196, 200, 400, 401, 466b, 466d, 469, 508, 660, 826b



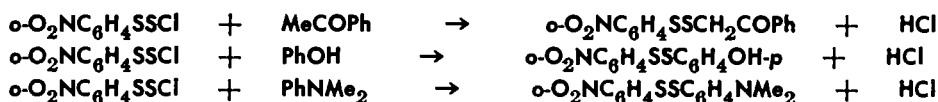
A sulfide-selenide may be made similarly: 662a



With pyridine as a catalyst a thiocyanate or a selenocyanate, reacts as a halide: 569b

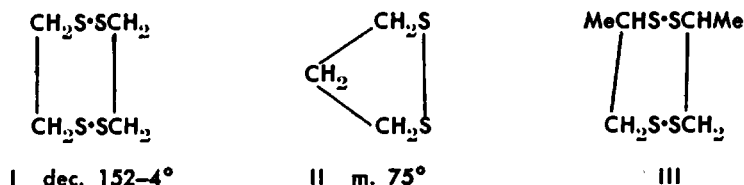


An aryl dithiochloride reacts with a ketone, a phenol,<sup>347</sup> or a dialkylaniline: 468



### Polymeric Disulfides

By treating ethylene<sup>230</sup> and trimethylene<sup>23</sup> dimercaptans with bromine, solids were obtained to which were assigned the structures I and II. Compound I was gotten in a roundabout way.<sup>598e</sup>



Trimethylene and propylene thiocyanates treated with alkali, gave II and III.<sup>336</sup> Compounds of the same composition as I were made in two other ways, one by the oxidation of ethylene dimercaptan<sup>230</sup> and the other by the reaction of ethylene bromide and sodium disulfide.<sup>85b</sup> This one melted at 113° and was considered to be different. All of them gave the same product on oxidation by nitric acid. These observations were made before the relationships of monomeric rings and linear polymers were understood. The fact that these compounds are solids should have aroused suspicion. They are closely related to polymers that

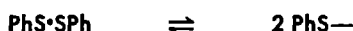
will be taken up in the chapter under thioelastomers. Cyclic monomeric disulfides are known and have been taken up in chapter 1. The trithiones have the three carbon two sulfur ring II.

### REACTIONS OF DISULFIDES

Reference should be made to the reviews on this subject.<sup>700c, 792</sup>

#### *Decomposition*

The sulfur-sulfur bond in a disulfide is very labile. It has been maintained that diphenyl disulfide dissociates into free radicals after the manner of hexaphenylethane: <sup>466a, 466c, 709, 711</sup>



Aryl disulfides are decomposed by ultraviolet light but the quantum yield is small.<sup>499</sup> Redistribution between two disulfides takes place under the influence of ultraviolet light: <sup>436a</sup>



This is assumed to be evidence of dissociation. Organic peroxides, which are believed to generate free radicals, also favor redistribution.<sup>436b</sup> The fact that a disulfide brings about the polymerization of acrylonitrile under irradiation by ultraviolet light has been considered as proof of dissociation. Diphenyl disulfide is more efficient than aliphatic disulfides in this.<sup>79</sup> This disulfide promotes the addition of a mercaptan to an unsaturate under the same influence.<sup>688</sup> This is additional evidence of dissociation. A substituted phenyl disulfide has been found to promote addition and polymerization.<sup>426,5</sup> Diphenyl disulfide and some of its substitution products are almost colorless in the crystalline form at room temperature but become colored when heated, either alone or in solution. The color deepens as the temperature rises.<sup>466a, 466c, 706a, 710</sup> Substituted dinaphthyl disulfides show thermochromic changes.<sup>567</sup> The existence of long-life radicals has been questioned.<sup>466f</sup> None of the expected mixed disulfide was found in a solution of two disulfides that had been heated.<sup>466c</sup> In more recent experiments unsymmetrical substituted phenyl disulfides disproportionated to the symmetrical when heated to 175°, or when boiled in dioxane, or when exposed to ultraviolet light. In a study of the influence of substituents on dissociation of twenty-four phenyl disulfides, the groups arranged themselves in the

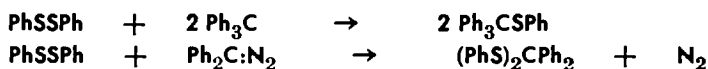
order,  $\text{AcNH} > \text{Cl} > \text{NO}_2 > \text{H} > \text{Me}$ .<sup>464</sup> The reaction of mercury with phenyl disulfide has been examined from both sides to determine the strength of the  $-\text{S}-\text{S}-$  bond:<sup>466f</sup>



The benzene solution of triphenyl methyl disulfide is yellow and takes up oxygen. The dissociation appears to be:<sup>86</sup>



Diphenyl disulfide reacts readily with triphenylmethyl and with diphenyldiazomethane:<sup>711, 712</sup>



Aliphatic disulfides are not very stable to heat. Dipropyl disulfide is about the highest that can be distilled at atmospheric pressure. The pyrolysis of an aliphatic disulfide gives a mixture which usually contains some of the mercaptan, some of the monosulfide, and some hydrogen sulfide.<sup>225</sup> Dienes may be formed.<sup>735</sup> The primary products of the pyrolysis of methyl disulfide appear to be methyl mercaptan and thioformaldehyde.<sup>169.5</sup> When cyclopentyl disulfide is passed over aluminum silicate at  $300^\circ$ , it breaks up into cyclopentyl mercaptan, cyclopentene, and other products.<sup>804b</sup> At  $280^\circ$  bornyl disulfide is transformed into thio-camphor.<sup>341</sup> Glycerol is said to prevent the formation of mercaptans in the distillation of hydrocarbons containing disulfides.<sup>25</sup>

Aromatic disulfides are considerably more stable. On distillation aryl disulfides are decomposed, one of the products being the corresponding mercaptan.<sup>174</sup> At  $270-300^\circ$ , diphenyl disulfide gives the monosulfide,<sup>317, 367d</sup> dibenzothiophene,<sup>317</sup> thiophenol, and thianthrene.<sup>708, 709</sup> At  $400^\circ$  *p*-tolyl disulfide gives some toluene and some *p*-cresyl mercaptan.<sup>804a</sup> The primary decomposition products of dibenzyl disulfide appear to be stilbene, hydrogen sulfide, and sulfur:<sup>272</sup>



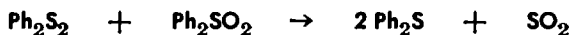
Diphenyl- and tetraphenyl-thiophene and other products are probably secondary.<sup>272</sup>  $\alpha$ -Phenylethyl disulfide,  $(\text{PhCHMeS})_2$ , decomposes similarly two diphenylthiophenes being among the products.<sup>51</sup> Dibenzhydryl disulfide,  $(\text{Ph}_2\text{CHS})_2$ , gives diphenyl-

methane and tetraphenylstilbene.<sup>858a</sup> Triphenylmethyl disulfide goes to pieces readily, as might be expected.<sup>86, 826a, 826b</sup> When *bis*-(*p*-hydroxyphenyl)disulfide is heated with sodium carbonate in glycerol to 190°, only one sulfur atom is lost.<sup>470a</sup> Several disulfides, heated with betaine, were transformed into methyl alkyl, or aryl, sulfides.<sup>147</sup> Heated with sulfur, benzyl disulfide gives 5-phenylbenzothiophene and tetraphenylthiophene.<sup>388</sup> The addition of sulfur to disulfides will be taken up later.

Diphenyl disulfide is decomposed by aluminum chloride into the monosulfide and other products.<sup>88</sup> Thianthrene may be formed.<sup>193</sup> Copper abstracts one of the sulfur atoms from *o,o'*-phenylene disulfide, leaving dibenzothiophene.<sup>42</sup> In general the desulfurization of polysulfides by metals stops at the disulfide stage but where the sulfur-carbon bond is weak as in the  $S_x(CH_2CO_2H)_2$  group it may go on to the monosulfide.<sup>540b</sup> Half of the sulfur is taken out of the allyl disulfide by lead amalgam,<sup>40</sup> or by zinc, but not out of methyl or ethyl disulfides.<sup>141b</sup>

Raney nickel, without hydrogen, removes half of the sulfur from aryl disulfides,<sup>351, 352</sup> while ordinary Raney nickel converts *p*-tolyl disulfide to toluene.<sup>559</sup> It removes all of the sulfur from dithiodiacetic acid.<sup>102</sup> Raney nickel takes all of the selenium out of aromatic diselenides.<sup>849</sup> All of the sulfur is taken out of a disulfide by catalytic hydrogenation over nickel<sup>38</sup> or other metal catalyst.<sup>384</sup>

There is a curious reaction between phenyl disulfide and diphenyl sulfone, when a mixture of the two is heated.<sup>451</sup>



Concentrated sulfuric acid converts phenyl disulfide to thianthrene.<sup>269</sup>

Unsymmetrical aryl disulfides react with 2,4-dinitrophenyl chloride to form 2,4-dinitrophenyl aryl disulfides.<sup>464</sup> Methyl disulfide and methyl iodide give trimethyl sulfonium iodide, which involves breaking the sulfur-sulfur bond.<sup>179, 727a, 762</sup> Mercuric iodide is a catalyst for this reaction.<sup>727a</sup> Ethyl disulfide reacts similarly but more slowly.<sup>693</sup> In one recorded experiment the union was not complete in three years at room temperatures.<sup>365</sup> It is not surprising that it has been missed. Diphenyl disulfide reacts in this way but very slowly.<sup>762</sup> Allyl disulfide

reacts more promptly with methyl iodide. The fact that methyl iodide removes sulfur as  $\text{Me}_3\text{SI}$  from vulcanized rubber has been considered as evidence of the presence of the disulfide linkage.<sup>726</sup> <sup>727a</sup> Benzyl iodide combines with benzyl disulfide and mercuric iodide to give  $(\text{PhCH}_2)_3\text{SI}\cdot\text{HgI}$ . With ethyl disulfide a mixed sulfonium salt is formed.<sup>332</sup> These reactions involve the breaking of a sulfur-carbon bond.

Benzyl disulfide and chloramine-B give the compound,  $\text{PhCH}_2\text{S}(\text{NHSO}_2\text{Ph})\text{:NSO}_2\text{Ph}$ .<sup>791</sup> Cyclohexyl disulfide reacts similarly.<sup>835b</sup> Yellow phosphorus combines with a disulfide to form a trialkyl trithiophosphite,  $(\text{RS})_3\text{P}$ .<sup>765</sup> Triphenylphosphine abstracts a part of the sulfur to make triphenylphosphine sulfide,  $\text{Ph}_3\text{PS}$ .<sup>707</sup>

An extensive study has been made by Challenger and coworkers of the transformation of alkyl disulfides and other sulfur compounds by microorganisms.<sup>138a, 139, 141a, 142</sup> This has been reviewed.<sup>138b</sup>

### Reduction

One of the most important facts about disulfides is the ease and completeness with which they can be reduced to mercaptans. The ease and completeness of the oxidation of mercaptans to disulfides is equally important. A mixture of a disulfide and a mercaptan may be considered an oxidation-reduction buffer, somewhat analogous to the well known acid-base buffers. When both are present a limited amount of oxidation, or of reduction, does not change the oxidation potential. The cystine-cysteine system may be involved in maintaining the oxidation-reduction balance in living organisms. This can be only glimpsed here.

Dithiodiglycolic acid serves as a catalyst in anaerobic oxidations.<sup>348</sup>

Propyl disulfide and decyl mercaptan reach an equilibrium state in 62 hours at  $139^\circ$  in a sealed tube.<sup>316</sup> As will be shown later, the equilibrium is established quickly in the presence of a mercaptide.

The reduction of disulfides to mercaptans has been considered in chapter 1, Volume I, as a method of preparing mercaptans. A few examples will be given here that involve sulfur compounds. Disulfides are reduced to mercaptans by sodium hydrosulfide,<sup>104, 216, 358, 515, 605</sup> sulfide,<sup>104, 494, 598b</sup> disulfide,<sup>104, 494, 623a</sup> or polysul-

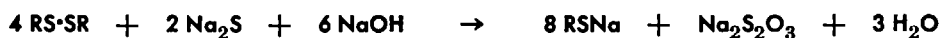
fide.<sup>358, 494</sup> An equation may be written which tells a part of the truth:



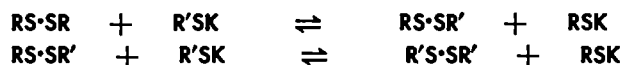
This is an equilibrium. Higher alkali polysulfides may convert mercaptans to disulfides<sup>380b</sup> and even add sulfur to the alkyl disulfides. The reversible electrolytic reduction of a disulfide has been written:<sup>784.5</sup>



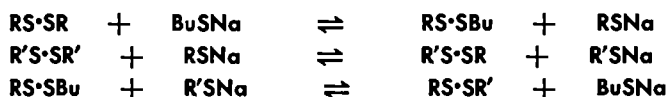
The reduction by sodium sulfide may be written:<sup>104</sup>



A disulfide reacts with a sodium mercaptide:<sup>466d</sup>



The reduction by *t*-butyl mercaptan is slow.<sup>79</sup> The redistribution of alkyl disulfides may be effected by catalytic amounts of a mercaptide:<sup>630a, 742</sup>



There is always some of a sodium mercaptide to carry on the reaction until equilibrium is reached. An alkali sulfide may serve the same purpose.<sup>629b</sup> The necessary sodium mercaptide may result from the action of sodium hydroxide and thiosulfate on the disulfides.<sup>401, 436b</sup>

Mercaptans and disulfides, in a solution, come to equilibrium with the formation of all possible disulfides and mercaptans. The removal of a volatile mercaptan causes a readjustment.<sup>12, 231</sup> The exchange between mercaptans and disulfides has been studied by the use of  $\text{S}^{80}$ .<sup>231, 328.5</sup> There seems to be a reversible equilibrium between cystine plus thiourea and cysteine plus S(guanyltio)-cysteine.<sup>809.5</sup>

In the presence of water, triphenyl phosphine reduces diphenyl disulfide to the mercaptan.<sup>706b</sup> Disulfides can be reduced by the dropping mercury electrode<sup>833.5</sup> or polarographically.<sup>338</sup> They may be reduced to the mercaptans by glucose,<sup>97.5, 153, 468</sup> sodium arsenite,<sup>331</sup> lithium aluminum hydride,<sup>21, 245</sup> or by hydrogenation



over molybdenum sulfide.<sup>545</sup> Cystine may be reduced by sodium bisulfite.<sup>7.5, 530.5</sup> Keratins may be modified by reducing the cystine linkages and bringing about reactions of the free mercapto groups.<sup>7.5, 313.3, 334, 335, 347.5, 347.7, 605.5</sup> Alkylation by a monoalkyl halide increases the extensibility but decreases the strength, with a dihalide it gives a product more like the original wool but less sensitive to alkali.<sup>605.5</sup> The reduction of cystine linkages, the basis of hair waving, has been considered in chapter 5, Volume I.

At 250° *i*-amyl<sup>673</sup> and phenyl<sup>446.5, 569a</sup> disulfides remove hydrogen from tetralin and are thereby reduced to the mercaptans. Isobornylaniline and amyl disulfide give amyl mercaptan and camphoranil.<sup>687</sup>

When sodium is placed in an ether solution of an alkyl disulfide, the mercaptide is formed:<sup>555</sup>



When sodium is added to a boiling alcoholic solution of benzyl disulfide the mercaptide is only one of several products.<sup>275</sup>

### Oxidation

The oxidation of a mercaptan to the sulfonic acid has been mentioned in chapter 2, Volume I. In this the disulfide may be considered an intermediate which may, or may not, be isolated. Nitric acid, particularly when hot, oxidises disulfides to sulfonic acids.<sup>66, 85a, 128, 178, 227, 362, 445, 566, 597c, 612, 694, 825</sup> The cold acid may give the "disulfoxide,"  $\text{RSO}_2\text{SR}$ .<sup>608, 694, 853</sup> This is obtained also by oxidation with sulfuric acid.<sup>67</sup> Electrolytic oxidation gives the sulfonic acid.<sup>120, 244</sup> Chromate and permanganate give this and sometimes the disulfone,  $\text{RSO}_2\cdot\text{SO}_2\text{R}$ .<sup>168</sup>

Oxidation by hydrogen peroxide may go to the sulfenic acid<sup>700a, 700c</sup> or may stop at  $\text{RSO}_2\text{SR}$ ,<sup>27, 112, 150, 367b, 699, 835b</sup> or the sulfinic acid,  $\text{RSO}_2\text{H}$ .<sup>514</sup> Perbenzoic acid gives lower oxidation products,  $\text{RSO}\cdot\text{SR}$ <sup>112, 136, 401</sup> or  $\text{RSO}_2\text{SR}$ .<sup>27</sup> Whether the oxidation product of an unsymmetrical aryl disulfide by a peracid is  $\text{ArSO}_2\text{SAr}'$  or  $\text{ArSSO}_2\text{Ar}'$  depends on the substituents on the aryls.<sup>464</sup> The oxidation product from phenyl disulfide is said to have anti-bacterial activity.<sup>640</sup> The rates of oxidation of several disulfides by benzoyl peroxide have been measured.<sup>387</sup> The cystine groups

in keratins may be oxidised by aliphatic <sup>7.5, 7.7, 8, 8.3, 8.5, 608.5, 842.5</sup> and inorganic <sup>206.5</sup> peracids.

Gaseous oxygen, containing a catalytic amount of nitrogen oxides, takes a disulfide to a mixture of the sulfonic acid and the disulfone.<sup>629a, 632, 758</sup> Selenium dioxide oxidises disulfides to sulfoxides and sulfones.<sup>528</sup>

Chlorine reacts with alkyl and aryl disulfides in various ways, according to conditions. The first product appears to be the sulfenyl chloride,  $\text{RSCl}$  or  $\text{ArSCl}$ , as has been discussed in chapter 3, Volume I. Under special conditions the sulfenyl chloride,  $\text{MeSCl}$ , can be obtained from methyl disulfide.<sup>114</sup> In sunlight the methyl groups are chlorinated to  $\text{Cl}_3\text{CS}\cdot\text{SCCl}_3$ .<sup>670</sup> In cold water the usual product is the sulfone chloride,  $\text{RSO}_2\text{Cl}$ .<sup>2, 70, 696b, 830, 864</sup> Ethyl disulfide may be oxidised to the sulfone chloride by chlorine in dry air containing nitric oxide.<sup>631</sup> It has been proposed to remove alkyl disulfides from gasoline by chlorination to the sulfenyl chlorides which are then taken out by a hot caustic wash.<sup>866</sup> At  $-20^\circ$  sulfuryl chloride converts methyl and ethyl disulfides to  $\text{ClCH}_2\text{SCl}$  <sup>113.5</sup> and  $\text{MeCHCl}\cdot\text{SCl}$ .<sup>113.3</sup>

Bromine appears to form an addition product,  $\text{RSBr}_2\cdot\text{SBr}_2\text{R}$  which is hydrolyzed to the "disulfoxide,"  $\text{RSO}_2\text{SR}$ .<sup>271b</sup> The oxidation by hypobromous acid has been studied.<sup>862, 863</sup> A bromide-bromate mixture may take a disulfide to the sulfone bromide,  $\text{RSO}_2\text{Br}$ .<sup>737</sup> If aluminum chloride is present, phenyl disulfide may be brominated to  $(\text{Br}_3\text{C}_6\text{H}_2\text{S})_2$ .<sup>787c</sup> *p*-Thiocresol may give the 3,3'-dibromo compound.<sup>872</sup>

### Hydrolysis

Disulfides are split by alkali. It is commonly stated that the first reaction is hydrolysis: <sup>206, 703.5</sup>



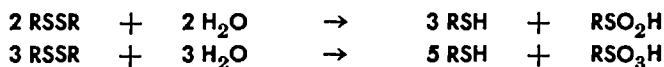
Benzyl dinitrophenyl sulfide was obtained when benzyl chloride was added to an alcoholic potash solution of 2,4-dinitrophenyl disulfide.<sup>273</sup>  $\text{RSO}_2\text{Na}$  is the sodium salt of a sulfenic acid. Sulfenic acid and its salts are unstable and disproportionation takes place: <sup>271a, 598d, 696b</sup>



This may go further:



The over-all hydrolysis may be written:



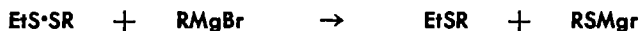
Other oxygenated products may be formed. Thus benzoic acid is found among the products of the hydrolysis of benzyl disulfide.<sup>627c</sup>

The tetramethyl derivative of dithiodiglycolic acid,  $(\cdot\text{SCMe}_2\text{COOH})_2$ , is stable to alkali but the tetraphenyl,  $(\cdot\text{SCPh}_2\text{COOH})_2$ , is not.<sup>701d</sup> From cystine half of the sulfur is taken out as hydrogen sulfide.<sup>280, 717</sup>

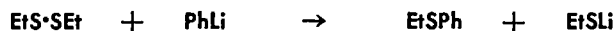
An entirely different mechanism for the splitting of disulfides by alkali has been proposed recently.<sup>684.5, 685</sup> This is based on the fact that some disulfides, such as *t*-butyl, are not affected by alkali. Cleavage seems to depend on the presence of a hydrogen atom on a carbon linked to the sulfur. It has been found that the ultraviolet absorption of disulfides, which have this hydrogen, shift with rise in pH while this is not the case where this hydrogen is lacking. It is assumed that the dissociation of this hydrogen in the presence of alkali leaves a carbanion from which the charge shifts to the adjacent sulfur atom which assumes a higher valence. The new anion breaks down into a thioaldehyde, or thioketone, and a mercaptan.

### Other Reactions

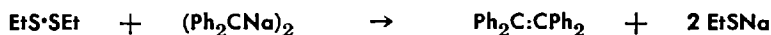
A Grignard reagent reacts with an alkyl disulfide:



The final products are the mixed sulfide and the mercaptan.<sup>462, 858b, 858c</sup> Phenyl lithium reacts similarly:<sup>713, 764</sup>



Phenyl magnesium bromide and a disulfide give the mixed sulfide and biphenyl.<sup>125</sup> The mixed sulfide  $\text{MeSCH}_2\text{CO}_2\text{Et}$  and free iodine are the products from methyl disulfide and iodoacetic ester.<sup>475</sup> The disodium derivative of *s*-tetraphenylethane and ethyl disulfide give tetraphenylethylene and sodium mercaptide:<sup>713</sup>



Butyl lithium and diphenyl disulfide give the 4,4'-dilithium derivative and butane: <sup>310</sup>



The addition of disulfides to unsaturates is a general reaction which should be exploited further.<sup>502</sup> Ethylene and ethyl disulfide, dissolved in anhydrous hydrofluoric acid, unite: <sup>502</sup>



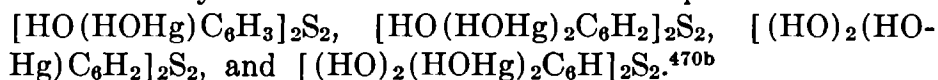
An alkyl disulfide and an olefin combine when heated together in the presence of a sulfactive hydrogenation catalyst. Thus butyl disulfide and ethylene give  $\text{BuSCH}_2\text{CH}_2\text{SBu}$ .<sup>738b</sup> Iodine is a catalyst for the addition of methyl disulfide to tetrafluoroethylene. The products are  $\text{MeS}(\text{CF}_2\text{CF}_2)_n\text{SMe}$ . A solid in which  $n = 10$ , m.  $113-6^\circ$ , has been isolated.<sup>339</sup> The addition of methyl disulfide to dodecene-1 is catalyzed by ethanesulfonic acid.<sup>629c</sup> Styrene takes up alkyl disulfides.<sup>381b</sup> Phenyl disulfide combines with maleic acid.<sup>630b</sup> Tung oil takes up allyl disulfide.<sup>454</sup> *p*-Tolyl disulfide and acetylene form 5-methylthianaphthene.<sup>690.5</sup>

Alkyl disulfides are taken out of gasoline by adsorption on silica gel <sup>342</sup> or bauxite.<sup>355</sup> They form adducts with urea.<sup>238</sup>

In the Willgerodt reaction a disulfide is converted to a thioamide.<sup>506</sup> This will be taken up in Volume IV under thioacids.

Disulfides form complexes with salts of platinum,<sup>152, 646, 647, 648</sup> mercury,<sup>80, 83, 146, 175, 645, 728</sup> gold,<sup>644, 728</sup> silver,<sup>749</sup> and iridium.<sup>645</sup> Methyl disulfide forms a complex with diborane.<sup>123.5</sup> 2,4-Dihydroxydiphenyl disulfide forms complexes with salts of heavy metals.<sup>470a, 714</sup> Copper naphthenate, added to a naphtha containing disulfides, forms complexes which are left in the still bottoms. It removes disulfides from hydrocarbon gases.<sup>385</sup>

Mono- and di-sulfides of phenol <sup>470a</sup> and of resorcinol <sup>470b</sup> are mercurated by mercuric chloride. Some of the products are:



*o*-Hydroxyphenyl disulfide loses a molecule of water readily, passing into the disulfide of phenyl ether,  $\text{O}(\text{C}_6\text{H}_4)_2\text{S}_2$ .<sup>325</sup>

#### ESTIMATION OF DISULFIDES

The methods of detecting and determining disulfides have been reviewed.<sup>155, 416.5</sup>

The customary method of estimation is to reduce them to mercaptans, which are then determined by appropriate methods.<sup>36, 62, 119, 293, 345, 390.5, 444, 473, 570, 724, 861</sup> The reduction is conveniently effected by zinc in acid solution. Mercaptans, if present, may be estimated beforehand and their amount subtracted. It has been proposed to get rid of the mercaptans by combining them with acrylonitrile before the reduction of the disulfides.<sup>207</sup> At a proper pH a disulfide may be reduced by thiosulfate or cyanide.<sup>700c, 704</sup>

Polarographic estimation of disulfides has been recommended.<sup>167</sup> The reduction potential of diphenyl disulfide is  $-0.5$  volt, while that of aliphatic disulfides is  $-1.25$  volt.<sup>299</sup>

A disulfide may be passed over alumina at  $650^{\circ}$  and the hydrogen sulfide determined.<sup>690</sup> Or it may be burnt over a platinum catalyst at  $900^{\circ}$  and finally weighed as barium sulfate.<sup>232</sup> In the known absence of other sulfur compounds the lamp method is satisfactory.<sup>831</sup>

Grote's reagent may be used for detecting alkyl disulfide.<sup>321</sup> At pH 10 this gives a purple-red color.<sup>753</sup> This can be adapted to chromatographic estimation.<sup>806</sup> Phosphotungstic acid is used in the estimation of cystine.<sup>416.6</sup>

An instrument has been constructed for the continuous, automatic titration of disulfides and other sulfur compounds in a gas stream.<sup>22</sup>

#### PHYSIOLOGICAL

The injection of propyl disulfide causes anemia.<sup>324, 847</sup> Methyl disulfide induces paralysis of the respiration of rats.<sup>484</sup> It exerts a lipotropic effect when administered peritoneally to young rats on a basal diet which produces fatty livers.<sup>676</sup> Ethyl and allyl disulfides have antiseptic action.<sup>432, 433</sup> The latter disulfide inhibits mitosis.<sup>376</sup> *p*-Nitrophenyl disulfide has some beneficial effect in mouse pneumonia.<sup>527</sup>

Quinolyl-,<sup>149, 843</sup> anthraquinolyl-, *o*-chlorobenzyl-, *p*-chlorobenzyl-, 3,4-dichlorobenzyl-, and 2,4-diaminobenzyl disulfides<sup>149</sup> have been tested as antimalarials. Ethyl disulfide was the most active of several tested against tuberculosis.<sup>120.5</sup>

4-Chlorobenzyl-, 2,4-dichlorobenzyl-<sup>803</sup> and 2,4-dichlorophenyldisulfide<sup>578</sup> and 2,5-dichlorophenylsulfonyl disulfide<sup>770</sup> have been tested as growth regulators for plants.

2-Chlorocyclohexyl disulfide prevents the growth of some types of carcinoma.<sup>333</sup>

## APPLICATIONS

Alkyl disulfides have been recommended for extracting oxygenated compounds from aqueous solutions in the Fischer-Tropsch process.<sup>411</sup> Some have been used in cutting oils.<sup>730, 867</sup> In lubricating oils<sup>718a</sup> various disulfides have been said to improve film strength<sup>222, 223, 481, 634</sup> and detergent action,<sup>832</sup> to prevent sludge formation,<sup>549</sup> inhibit corrosion,<sup>122, 820</sup> stabilize<sup>535, 746</sup> and serve as antioxidants.<sup>117a, 122, 465</sup> Details of specific recommendations can not be given here. Propyl disulfide is a stabilizer for pure hydrocarbons.<sup>552</sup> Butyl, *i*-amyl, and methylphenyl disulfides stabilize petroleum wax.<sup>281</sup> Several aromatic disulfides are stabilizers for photographic emulsions.<sup>560</sup> Allyl disulfide prevents injury to films by heat and light.<sup>519</sup> The addition of disulfides from petroleum distillates to viscose for spinning has been recommended.<sup>633</sup>

Disulfides are antagonistic to lead tetraethyl.<sup>483</sup> Injected into engine fuels they are said to prevent carbonization of metal parts.<sup>819</sup> Their addition to Diesel fuels has been suggested,<sup>356, 419, 585, 586</sup> but their use is limited on account of corrosion. Certain disulfides are claimed as flotation agent.<sup>556</sup>

Treating dehydrated castor oil with small amounts of alkyl disulfides improves films which it forms.<sup>164</sup> Disulfides have been used as constituents of resins,<sup>414</sup> particularly in phenol-formaldehyde.<sup>553, 682</sup>

Aryl disulfides promote the photopolymerization of olefins.<sup>397, 669</sup> Butyl disulfide is a catalyst for the addition of thioacetic acid to vinyl fluoride.<sup>220</sup> Amyl disulfide aids in the addition of a mercaptan to vinyl chloride under the influence of ultraviolet light.<sup>689</sup> Phenyl disulfide is even better for this purpose.<sup>688</sup> They serve as regulators in emulsion polymerization.<sup>319</sup> They catalyze the oxidation of sodium azide by iodine but are less effective than mercaptans.<sup>24</sup>

Various disulfides have been suggested as solvents,<sup>845</sup> reclaiming agents,<sup>219</sup> softeners,<sup>606</sup> plasticizers,<sup>181, 746, 836</sup> and modifiers<sup>205</sup> for different kinds of rubbers. They act as vulcanization accelerators<sup>124</sup> but are less active than the corresponding mercaptans.<sup>56</sup>

The use of tolyl disulfides in beauty preparations has been mentioned.<sup>797</sup>

The disulfides from petroleum distillates have been claimed as pesticides.<sup>656</sup> Methyl disulfide is effective against nematode larvae<sup>148</sup> and methyl-allyl against blow flies.<sup>487a</sup> Methyl and

ethyl disulfides combat weevil in wheat.<sup>674</sup> Butyl disulfide has been compared with several other pesticides.<sup>208, 487b</sup> Synergism between *p*-chlorophenyl disulfide and nicotine has been demonstrated.<sup>522</sup> Octyl disulfide has been used with nicotine against melon worms.<sup>523</sup> Aryl disulfides are recommended for use in fly sprays,<sup>771</sup> in tree sprays,<sup>509</sup> and for dusting wheat to destroy rust.<sup>395a</sup> Amino-aryl disulfides are claimed as fungicides.<sup>458</sup>

*t*-Octyl disulfide is effective as a defoliant.<sup>315</sup>  $\beta$ -Phenylacetyl-aminoethyl disulfide is a precursor of penicillin.<sup>60</sup> Methyl disulfide appears to be coming into use as an odorant for natural gas. Hydroxy- and amino-phenyl disulfides can be coupled with diazonium compounds to form dyes.<sup>285</sup>

A disulfide reagent, 2,2'-dihydroxy-6,6'-naphthol disulfide, has been recommended as a reagent for determining the presence of mercaptan groups in proteins.<sup>44,5</sup>

## Disulfide Acids

### ALIPHATIC DISULFIDE ACIDS

In their preparation and in their reactions the disulfide acids present little that is novel or unexpected. There are two general methods of preparation, the oxidation of mercapto-acids, which has been taken up in chapter 5, Volume I, and the reaction of haloacids with sodium disulfide, which is similar to that of alkyl halides as has been discussed earlier in this chapter.

Since the disulfide and carboxyl groups do not interfere with each other the disulfide acids have two sets of reactions which are practically independent.

Dithiodiglycolic acid,  $(\text{SCH}_2\text{CO}_2\text{H})_2$ , the simplest and best known member of this class has been made from chloracetic acid and sodium<sup>85a, 263, 284, 415b</sup> or calcium<sup>415a</sup> disulfide. It can be obtained by the oxidation of the Bunte salt by iodine<sup>775a</sup> or electrolytically.<sup>624</sup> This holds for other acids of this group.<sup>627a, 775a</sup> Thioglycolic acid is oxidised by phenacyl bromide which is reduced to acetophenone.<sup>380e</sup>

The acid chloride results from the addition of ketene to sulfur chloride:



Substituted ketenes react similarly.<sup>343, 583, 584</sup>

Treating methyl<sup>565</sup> and butyl<sup>226</sup> acrylates with sodium tetrasulfide converts them to esters of  $\beta,\beta'$ -dithiodipropionic acid,  $S_2(CH_2CH_2CO_2R)_2$ . Disulfide acids are obtained similarly from maleic and crotonic acids.<sup>565</sup> Acrylonitrile goes to the disulfide nitrile,  $S_2(CH_2CH_2CN)_2$ .<sup>226</sup>

Dithiodilactic,  $(\cdot SCHMeCO_2H)_2$ ,<sup>91, 261c</sup> and  $\alpha,\alpha'$ -dithioundecylic,  $(\cdot S(CH_2)_{10}CO_2H)_2$ ,<sup>186</sup> acids have been made from the haloacids and sodium disulfide. The optically active forms of dithiodilactic acid have been prepared.<sup>261c, 261d</sup> This acid has been made starting with pyruvic acid and hydrogen sulfide.<sup>491c</sup>

The meso, racemic, and the two optically active forms of  $\alpha,\alpha'$ -dithiodibutyric acid have been prepared.<sup>4</sup>  $\gamma,\gamma'$ -dithiodibutyric,  $(\cdot SCH_2CH_2CH_2CO_2H)_2$ , has been made by way of the nitrile<sup>287</sup> and also in a round-about way starting with cyanoacetic ester and ethylene sulfide.<sup>750</sup> A dithioacid has been prepared from dimethyl- $\alpha$ -thiopyruvic acid by treating it with iodine.<sup>511</sup> Dithioglyceric acid,  $(\cdot SCH_2CH(OH)CO_2H)_2$  is produced by the air oxidation of the mercapto-acid.<sup>441</sup> A disulfide acid is made from malonic ester and sulfur chloride.<sup>852</sup>

An interesting disulfide acid is the cyclic  $\alpha$ -lipoic acid,  $CH_2CH_2CHCH_2CH_2CH_2CH_2COOH$ , which is taken up in chap-



ter 1 on cyclic sulfides.

Dithiodiglycolic acid is a regular acid. High yields of its esters, up to cetyl, have been obtained by refluxing it with a slight excess of the alcohol in toluene with *p*-toluenesulfonic acid as a catalyst.<sup>224, 564</sup> It can be converted to the chloride from which the amide and esters may be made.<sup>326</sup>

Disulfide acids can be reduced to mercapto-acids by the methods appropriate for alkyl and aryl disulfides.<sup>196, 461, 620</sup> The oxidation-reduction potential for the system thiolactic-dithiodilactic has been calculated from thermal data.<sup>99</sup> The equilibrium between dithiodiglycolic acid and the sulfide ion has been determined polarographically.<sup>779.5</sup>

The oxidation of a disulfide acid may go all the way to a sulfonic acid.<sup>210, 700a</sup> A curious case of disproportionation is the conversion of three molecules of dithiodipropionic acid,  $(\cdot SCH_2CH_2COOH)_2$ , into five of the mercaptide,  $BrHgSCH_2CH_2CO_2H$ , or  $AgSCH_2CH_2COOH$ , and one of the sulfonic acid,  $HO_3SCH_2-$



$\text{CH}_2\text{COOH}$ , by treatment with mercuric bromide, or with silver sulfate.<sup>621</sup> The oxidation of several disulfide acids by hydrogen peroxide in dioxane solution, has been studied.<sup>775b</sup> The air oxidation of barium thioglycolate does not stop at the disulfide stage but goes all the way to barium oxalate.<sup>701a</sup>

The hydrolysis of a disulfide acid appears to be similar to that of other disulfides, the immediate products possibly being the mercapto-acid and a sulfenic acid.<sup>700b, 701c, 702, 703</sup>

Disulfide acids may be estimated by bromide-bromate titration.<sup>357</sup>

The dissociation of dithiodiglycolic acid has been determined in a study of dibasic acids.<sup>834</sup> The affinity constant for this acid is  $K = 0.090$ , for dithiodilactic,  $0.080$ , and for  $\beta,\beta'$ -dithiodipropionic,  $0.0090$ .<sup>491a</sup> The proximity of the sulfur to the carboxyl makes a considerable difference. The conductivity of dithiodiglycolic acid in absolute alcohol has been measured.<sup>485</sup>

#### AROMATIC DISULFIDE ACIDS

The best known of this class are the three disulfide benzoic acids,  $(\text{HO}_2\text{CC}_6\text{H}_4)_2\text{S}_2$ , of which the di-ortho acid is the most important. It can be prepared by the oxidation of thiosalicylic acid.<sup>622</sup> Chloric acid<sup>395c</sup> and sulfuric acid<sup>16</sup> have been used as oxidising agents. It has been obtained by the partial reduction of *o*-benzoicsulfonyl chloride<sup>413</sup> and has been made by the reaction of diazotized anthranilic acid on sodium polysulfide,<sup>9</sup> or on a sulfantimonate, a sulfarsenate, or a sulfostannate.<sup>32a</sup> The 4-nitro-<sup>3, 731</sup> and 4-bromo-<sup>563</sup> acids have been made by the diazo reaction from substituted anthranilic acids. The 4-nitro acid has been made also from 2-thiocyano-4-nitrobenzoic acid.<sup>763</sup> The carboxyl group may be introduced into phenyl disulfide<sup>310</sup> or into thiophenol.<sup>305</sup> This disulfide acid has been obtained in more complicated reactions.<sup>15</sup>

The meta acid has been made by the diazo reaction<sup>35</sup> and by the reduction of the sulfonyl chloride.<sup>105, 745</sup> An amino derivative has been obtained from a benzothiazole.<sup>96</sup> The para disulfide acid,  $(p\text{-HO}_2\text{CC}_6\text{H}_4\text{S})_2$ , has been prepared by the diazo reaction.<sup>35, 802</sup>

5-Mercaptosalicylic acid has been oxidised to the disulfide acid,<sup>417</sup> which has been obtained also by the reduction of the corresponding sulfonyl chloride.<sup>767</sup>

The 4-disulfide acid has been made by treating an ester of 3-hydroxy-2-naphthoic acid with thionyl chloride.<sup>407</sup>

The presence of the disulfide group in the disulfide acids,  $(\text{HO}_2\text{CC}_6\text{H}_4)_2\text{S}_2$ , modifies only slightly the reactions of the carboxyls. Some of the reactions here listed are assumed to be characteristic of ortho, meta, and para isomers though examples for all three isomers have not been found in the literature.

These acids form stable, water-soluble salts with ammonia and amines.<sup>495</sup> Thionyl chloride converts them to the acid chlorides<sup>503</sup> from which amides,<sup>503</sup> N-alkylamides,<sup>46</sup> and esters<sup>474</sup> can be made. Phosphorus pentoxide dehydrates the amides to the nitriles.<sup>503</sup> The para acid decomposes at  $320^\circ$ .<sup>743</sup> Of course these derivatives can be made by oxidising the corresponding derivatives of the mercapto-acids.<sup>416,7</sup>

As disulfides they can be reduced to the mercapto-acids. Iron powder with sodium carbonate<sup>802</sup> and zinc in acetic acid<sup>9</sup> have been used for the reduction.

The meta acid has been oxidised by iodine and potassium iodide to the "disulfoxide."<sup>745</sup>

The disulfide linkage is broken by sodium hydroxide as has been described above for other disulfides.<sup>105, 743</sup>

Concentrated sulfuric acid converts a mixture of dithiodiglycolic acid and the ortho disulfide acid into the mixed disulfide acid,  $o\text{-HO}_2\text{CC}_6\text{H}_4\text{SSCH}_2\text{CO}_2\text{H}$ .<sup>744</sup> Under similar conditions condensations take place with benzene, toluene, anisole, and the three cresols. The respective products are thioxanthone,<sup>622</sup> 2-methylthioxanthone,<sup>16, 622</sup> 2-methoxythioxanthone,<sup>622</sup> and three hydroxymethylthioxanthones.<sup>729</sup> Condensations with acetic<sup>46, 256</sup> and propionic anhydrides give substituted thionaphthenes.<sup>203</sup> A benzothiazoline is formed when a halogen is added to a carbon tetrachloride solution of the N-diethylamide of the same acid.<sup>46</sup> The amide, benzaldehyde, and acetic acid give a benzothiazine.

#### PHYSIOLOGICAL

Several dithioacids have been tested as antidotes for hydrocyanic acid<sup>354</sup> and several as substitutes for cystine in which they failed.<sup>840</sup> The toxicities of dithiodiglycolic and thiodiglycolic acids have been determined.<sup>185</sup> The germicidal properties of the soaps of a series of  $\alpha, \alpha'$ -disulfide acids have been compared. The most effective are those from the lauric and myristic.<sup>214</sup>

Small doses of the sodium salt of *o,o'*-dithiodibenzoic acid lowered the blood pressure in a dog, slowed the heart, and accelerated respiration. The lethal dose was 0.3 g. per kilo. For the magnesium salt it was 0.1 g. per kilo.<sup>189</sup> Small doses arrested, while large doses of the sodium salt increased the normal movements of the dog intestine.<sup>190</sup> Mercury dithiosalicylate is markedly antiseptic. It stimulates prompt healing of lesions without irritation.<sup>571</sup>

### Aminodisulfides

$\beta,\beta'$ -Diaminodiethyl disulfide,  $(\text{H}_2\text{NCH}_2\text{CH}_2\text{S}\cdot)_2$ , has been of interest on account of its connection with cystine, from which it may be obtained by pyrolysis.<sup>577</sup> The starting material for its synthesis has been  $\beta$ -bromoethylphthalimide,  $\text{C}_6\text{H}_4(\text{CO})_2\text{NCH}_2\text{CH}_2\text{Br}$ . This may be converted to the mercaptan which is then oxidised to the disulfide.<sup>110, 163, 288, 471</sup> Another route is to make the thiocyanate and treat this with alkali.<sup>162</sup> Finally the imide is hydrolyzed. The aminomercaptan is also obtained by the hydrolysis of a thiazoline.<sup>291, 786</sup> Ethylene imine and hydrogen sulfide give the aminomercaptan,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$ , which can be oxidised.<sup>538</sup> The disulfide can be hydrogenated to the mercaptan over palladium sponge in hydrochloric acid.<sup>68</sup> The N-alkylated compound,  $(\text{Et}_2\text{NCH}_2\text{CH}_2\text{S}\cdot)_2$ , has been prepared by oxidation of the mercaptan.<sup>482</sup> Bromocholine disulfide results from the oxidation of thiocholine bromide.<sup>340</sup>

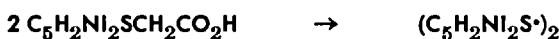
The next higher member of this series,  $(\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{S}\cdot)_2$ , has been made by the Gabriel synthesis.<sup>290</sup> Oxidation products, "disulfoxides" of the series,  $[\text{H}_2\text{N}(\text{CH}_2)_n\text{S}\cdot]_2$ , in which  $n = 1$  to 4, are said to have therapeutic value.<sup>150</sup> The pentamethylene disulfide was made from the chloride,  $\text{PhCONH}(\text{CH}_2)_5\text{Cl}$ , and sodium disulfide.<sup>249</sup> The dimethylamino pentamethylene disulfide, from the oxidation of the mercaptan, is said to have curare-like activity.<sup>375.5, 553, 554</sup>

Bromocholine disulfide results from the oxidation of thiocholine bromide.<sup>340</sup>

Various aminophenyl disulfides and their acyl derivatives have been made by oxidation of the mercaptans.<sup>242, 539, 829, 873, 876</sup> The formation of aminophenyl disulfides from thiocyanates<sup>92b, 418, 720</sup> must involve the oxidation of mercaptan intermediates. Alkylaminophenyl mercaptans are oxidised by air to the disulfides.<sup>431</sup>

Many amino-aromatic disulfides have been prepared by reducing the corresponding nitro compounds.<sup>396, 427, 460, 541, 618, 672, 789</sup> This serves for the preparation of the ortho and para compounds. Heating aniline, or its hydrochloride, with sulfur gives a mixture of the ortho and para disulfides along with mono- and trisulfides.<sup>325, 368a, 368b, 369, 377, 378, 607</sup> More of the ortho is formed at low temperatures, while higher favor the para.<sup>368b</sup> Improved laboratory methods have been given for the preparation of aniline and toluidine disulfides.<sup>736</sup> When *o*-toluidine is heated with sulfur, it is sulfurized in the 2 and 5 positions. The 2,2'-disulfide goes directly into a thiazole while the 5,5'-disulfide is isolated as such.<sup>370</sup> *o*-Amino-disulfides may be obtained from thiazoles.<sup>96, 692, 784</sup> *p*-Acetaminophenyl disulfide is formed when acetanilide and sulfur monochloride are heated together in acetic acid solution.<sup>734</sup> It has been maintained that this compound exists in three forms.<sup>367c, 427</sup>

A curious reaction is the formation of 3,5-diiodo-4-pyridyl disulfide from the corresponding mercaptoacetic, or mercaptopropionic, acid in alkaline solution: <sup>437</sup>



An amino-alkyl disulfide and an alkylisothiuronium salt give a bis-( $\omega$ -guanidinoalkyl) disulfide,  $[\text{H}_2\text{NC}(:\text{NH})\text{NH}(\text{CH}_2)_n\text{S}]_2$ .<sup>195</sup>

*o*-Aminophenyl disulfide and its *N*-dimethyl derivative form addition compounds with trinitrobenzene.<sup>783</sup> *o*-Aminophenyl disulfide reacts with ethyl oxalate to form the anilic ester which reacts further with ammonia and other amines.<sup>95a</sup> One of the two sulfur atoms of *o*-aminophenyl disulfide is removed by heating it with litharge in aniline.<sup>368c</sup> This disulfide forms anils with aldehydes.<sup>94</sup> The aminophenyl disulfides can be acetylated and benzoylated.<sup>427</sup>

The *o*-aminophenyl disulfide forms the succinanylic acid,  $(\cdot\text{SC}_6\text{H}_4\text{NHCOCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , with succinic anhydride. It replaces one of the sulfonic acid groups of methanedisulfonic acid giving the sulfonic acid disulfide,  $(\cdot\text{SC}_6\text{H}_4\text{NHCH}_2\text{SO}_3\text{H})_2$ .<sup>618</sup>

Both ortho and para give color reactions with ferric chloride and other oxidising agents.<sup>373</sup> Dyes have been made from them.<sup>675</sup> Both ortho and para and their acetyl and benzoyl derivatives lower the viscosity of a toluene solution of rubber.<sup>396</sup>

The half-wave potential of the ortho disulfide in a buffered solution has been studied.<sup>788</sup>

Certain  $\beta$ -alkylamino- and  $\beta$ -aryl-amino-ethyl disulfides cause lowering of blood pressure.<sup>111</sup>  $\beta$ -Aminoethyl disulfide known as cystamine, is said to protect against ionic radiations.<sup>752</sup>

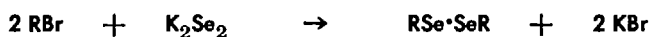
*o*-Aminophenyl disulfide, called intramine, has been of considerable pharmacological interest.<sup>368d</sup> It has been found useful in the treatment of syphilis.<sup>349, 504, 505</sup> Its acetyl and succinyl derivatives have been found to be active against infections.<sup>572, 617, 619</sup> Its formaldehyde sulfoxalate derivative has been used in combating bacterial infections.<sup>686</sup> Intramine is effective against *Staph. aureus*<sup>807</sup> and has been used in India with success against several infections.<sup>772</sup> It inhibits the metamorphosis of tadpoles but accelerates the growth of lupin plants.<sup>524</sup>

The bacteriostatic properties of some twenty substituted aminophenyl disulfides have been studied.<sup>850</sup>

## Diselenides



These resemble the disulfides, both as to methods of preparation and reactions. A selenomercaptan can be oxidised to the diselenide.<sup>639</sup> Chlorpicrin may be the oxidising agent.<sup>421</sup> Oxidation of a seleno Bunte salt,  $\text{RSeSO}_3\text{Na}$ , gives a diselenide.<sup>625, 815</sup> An alkyl halide reacts with an alkali diselenide: 28, 82, 93, 191, 601, 614, 755a



Diselenides are made from selenocyanates<sup>41, 59, 261a, 297, 423, 639, 684</sup> and from selenenyl halides,  $\text{RSeCl}$ ,  $\text{RSeBr}$ ,<sup>254a, 662b, 667</sup> or  $\text{RSeSCN}$ .<sup>662b</sup> Chloromethyl diselenide,  $(\text{ClCH}_2\text{Se})_2$ , is one of the products of the chlorination of trimeric selenoformaldehyde,  $(\text{CH}_2\text{Se})_3$ .<sup>113</sup> Chlorination of carbon diselenide in carbon tetrachloride yields  $(\text{Cl}_3\text{CSe})_2$ .<sup>399.5</sup> By coupling diazotized anthranilic acid with sodium polyselenide a high yield of the diselenide is obtained.<sup>705</sup> The addition of selenium to a Grignard reagent gives the diselenide along with the selenomercaptan.<sup>550, 787a</sup>

Diselenide acids require no special treatment as in their preparation and reactions they are so like other diselenides. In addition they have the characteristics of acids. Esters and amides

can be made from the acid chlorides.<sup>474</sup> The three diselenobenzoic acids have been prepared by the diazo reaction from the corresponding aminoacids.<sup>35, 474</sup>

Diselenides are reduced to selenomercaptans by sodium in alcohol<sup>82, 449</sup> or in liquid ammonia.<sup>161</sup> Zinc in boiling sodium hydroxide solution has been used for the reduction of the para diselenobenzoic acid.<sup>35</sup> By disproportionation in the presence of mercuric chloride diselenodilactic acid gives the chloromercury selenide,  $\text{RSeHgCl}$ , and the seleninic acid.<sup>261a</sup>

Diselenides are oxidised to seleninic,<sup>601, 662b</sup>  $\text{RSeO}_2\text{H}$ , or to selenonic,  $\text{RSeO}_3\text{H}$ <sup>474</sup> acids.

Of the diselenides studied the propyl proved to be the most stable to hydrolysis.<sup>601</sup>

Cinnamic acid is reduced to hydrocinnamic by boiling it with tetralin and phenyl diselenide.<sup>550</sup>

The dipole moment of  $\text{PtCl}_2(\text{Et}_2\text{Se}_2)_2$  has been determined.<sup>410</sup>

Aliphatic diselenides have been recommended as oxidation inhibitors.<sup>191</sup>

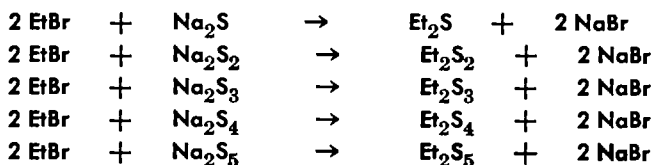
When a diseleno-acetic, or butyric, acid is injected into a mouse the highest selenium content is found in the lungs. If the mercury salt is injected the selenium goes to the kidneys.<sup>329</sup>

## Polysulfides

### FORMATION

Alkyl and aryl monosulfides are easy to prepare and are stable, well characterized compounds. As has been shown in the section just before this, much the same can be said of the disulfides. Mixtures containing polysulfides are easy to obtain but the isolation, purification, and characterization of individual tri- or tetrasulfides is difficult. In many cases clean cut separations are impossible.

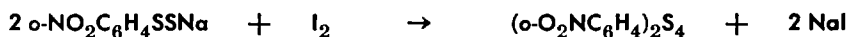
After making monosulfides and disulfides by the reactions of alkyl halides with sodium sulfide and disulfide, it was logical for the early chemists to try sodium polysulfides:



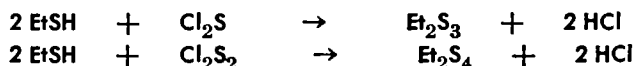
It has been pointed out already that this method is not altogether reliable even for disulfides since sodium disulfide is an equilibrium mixture of several sulfides. It is much worse with the higher sulfides of sodium where there are more possibilities. Alkyl monosulfides and disulfides can be purified by fractionation but this is seldom possible with the higher sulfides.

There is some doubt about the existence of alkyl hexasulfides though several have been reported.<sup>426</sup>

A number of investigators have made polysulfides from alkali polysulfides<sup>179, 194, 374, 395b, 595a, 610, 671, 778a</sup> and from ammonium polysulfides.<sup>380b, 801</sup> Allyl iodide reacts satisfactorily with anhydrous potassium pentasulfide.<sup>801</sup> *o*-Nitrophenyl tri- and tetrasulfides are from *o*-nitrophenyl chloride and the sodium polysulfides. The tetrasulfide was obtained also in another way:<sup>85c</sup>

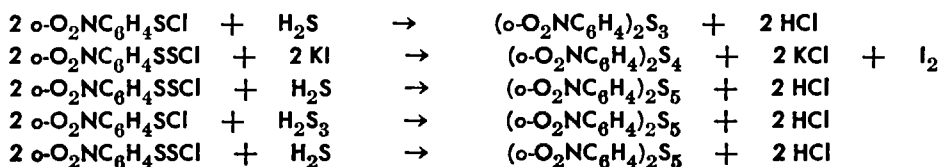


Another approach is the use of sulfur chlorides with mercaptans:



This looks neat but the chlorides of sulfur are equilibrium mixtures. Sulfur dichloride may contain free chlorine along with some sulfur monochloride so that the product may contain di- and tetrasulfides along with the desired trisulfide. Likewise sulfur monochloride gives mixtures. However, this method has been used extensively with fair results.<sup>34, 71, 79, 87, 117b, 137, 156, 209, 230.5, 286, 303, 435a, 467, 477a, 479a, 590, 604, 659, 749, 810, 814, 839</sup> Tri- and tetrasulfides have been made from mercaptobenzoic acids in this way.<sup>211, 212, 734</sup> A slight variation is the use of a lead mercaptide, instead of the mercaptan.<sup>72, 595b</sup> Sulfur dioxide,<sup>749</sup> or thionyl chloride,<sup>795</sup> may be substituted for the sulfur chloride without much change in the results. This method is applicable to both alkyl and aryl mercaptans.

Polysulfides have been made by the use of aromatic sulfenyl chlorides:<sup>347</sup>



Aliphatic sulfenyl chlorides react similarly.<sup>113,7</sup> The reactions of sulfenyl chlorides have been discussed in chapter 3, Volume I.

As was brought out in the chapter on mustard gas in chapter 5, Volume II, polysulfides are formed, along with monosulfides, by the addition of sulfur chloride to unsaturates.<sup>169, 283, 738a</sup>

A third method is useful when the aim is to get high sulfur content rather than to prepare an individual compound. This is the direct addition of sulfur to a disulfide, or to a lower polysulfide. The addition of sulfur to an alkyl, or aryl, monosulfide is not practicable though it does take place under drastic conditions. Some disulfide and trisulfide are formed when ethyl monosulfide is heated with sulfur to 180° for 24 hours.<sup>90</sup> Ethyl disulfide took up additional sulfur when it was heated with sulfur for twenty-four hours at 135° in a sealed tube.<sup>813</sup> *t*-Butyl disulfide takes up sulfur at 107–62°. <sup>718b</sup> Sulfur is taken up readily by an alkyl disulfide <sup>691, 719</sup> in the presence of alkali, <sup>833</sup> of ammonia, <sup>380b, 435a, 562, 842</sup> of amine, <sup>452, 589</sup> or of zinc oxide.<sup>87</sup> This will come up again under thioelastomers. Sulfur is taken up rapidly by a warm, stirred solution of ethyl disulfide containing 1% of triethylamine.<sup>652.5</sup> Phosphorus pentasulfide may serve as carrier.<sup>497</sup>

There are various special methods. A Grignard reagent reacts with sulfur chloride to give a disulfide and trisulfide among other things.<sup>235</sup>

When glycerol is heated with sulfur at 300° some allyl trisulfide is among the products.<sup>426</sup> Heating 1-methylcyclohexene with sulfur gives a mixture of polysulfides.<sup>229</sup> This will be taken up later. Heating 2,4-diaminoacetanilide with sulfur gives a trisulfide.<sup>408</sup>

The  $\alpha,\alpha'$ -trisulfide of propionic acid has been obtained by treating pyroracemic acid with hydrogen sulfide.<sup>491c</sup> Trifluoromethyl trisulfide is obtained by heating iodine pentafluoride with carbon disulfide. Sulfur and trifluoromethyl iodide give the tetrasulfide.<sup>350.5</sup>

### STRUCTURE

There has been much discussion as to the structure of the sulfur groups in polysulfides. This has come up in chapter 5 on mustard gas in Volume II and will be taken up under thioelastomers, in a later volume. The whole idea of structure in organic chemistry is based on the fixedness of bonds. As sulfur to sulfur



bonds are labile a group of sulfur atoms can not have a fixed structure.

There can be no doubt that there is a sulfur atom attached to each alkyl by a fixed bond so the only question is the disposition of the remaining sulfur atom, or atoms. Much has been made of the fact that sulfur can be added to a disulfide or removed from a tri- or tetrasulfide. This has been construed as favoring the idea that the extra sulfur is added to one of the sulfur atoms of the disulfide instead of being inserted between them. This argument loses its force when the lability of the sulfur to sulfur bonds is considered. Various structures have been proposed <sup>72, 182, 197, 198, 477a, 600</sup> but are not to be taken too seriously.

The question of the structure of polysulfides has been reviewed.<sup>71, 129</sup> It has been claimed that by oxidation, ethyl trisulfide, tetrasulfide, and pentasulfide are all converted to the trisulfoxide, EtSO·SO·SOEt, which was taken as establishing the basic structure, EtS·S·SEt, in all of them.<sup>44</sup> In view of the known lability of sulfur to sulfur bonds this does not seem to be proven.

This lability is manifested in chemical reactions and may have little or nothing to do with the validity of conclusions deduced from physical measurements.<sup>34, 156, 440, 855</sup> It is claimed that electron <sup>253, 350.5</sup> and x-ray diffraction data, Raman,<sup>253</sup> ultraviolet,<sup>253, 350.5</sup> and x-ray emission spectra indicate zigzag sulfur chains as opposed to conclusions from dipole moments, parachors, and viscosities which are considered less reliable.<sup>253</sup> A two-fold axis of symmetry, shown by x-rays, appears to exclude sulfur atoms attached to the chain.<sup>182</sup> From a study of the crystal structure of β,β'-diiododiethyl trisulfide it is concluded that the zig-zag chain is the correct one.<sup>183</sup>

The chain structure has been considered likely as it would naturally result from the various methods of formation<sup>347</sup> but it is not safe to exclude possible isomerization.

Some recent experiments with radioactive sulfur are of interest. This was added to ethyl trisulfide:



The resulting tetrasulfide was split by vacuum distillation into the trisulfide and sulfur. This trisulfide was radioactive. The disulfide obtained from it by treatment with alkali was inactive. This shows that the two sulfur atoms, linked to the two ethyl

groups, have taken no part in the exchange. Inactive ethyl tetrasulfide was heated with active ethyl trisulfide at 100° for 2 hours. Separation by vacuum distillation gave active trisulfide and active tetrasulfide. Active ethyl trisulfide,  $\text{Et}_2\text{S}_2\text{S}^*$ , was heated at 210° for 4 hours. The  $\text{Et}_2\text{S}_2$  obtained from this was inactive. These experiments show the fixedness of sulfur to carbon bonds and the complete lability of sulfur to sulfur bonds.<sup>328</sup> Similar experiments have been carried out with ethyl trisulfide and *p*-tolyl trisulfide.<sup>327</sup> In the exchange between disulfides and trisulfides the RS-group remains intact.<sup>328,5</sup>

In a recent study sulfur was extracted from samples of benzyl polysulfide prepared by different methods. In two cases the sulfur content of the residue was near that of the sulfide while in others it corresponded to that of the disulfide. More sulfur was taken out of a sample of benzyl tetrasulfide that had been heated than from the unheated material.<sup>53</sup> It is risky to draw conclusions from these few data on benzyl polysulfides in which the carbon to sulfur is notably labile.

#### REACTIONS OF POLYSULFIDES

The most characteristic reaction of polysulfides is the taking up of sulfur by the lower and the giving up of sulfur by the higher. In ultraviolet light methyl trisulfide gives some di- and tetrasulfides.<sup>79</sup> The polysulfides are all unstable at higher temperatures. For this reason only a few of the lower alkyl polysulfides can be distilled, even in a high vacuum. When an attempt is made to distill either phenyl tetrasulfide or pentasulfide at 1 mm., what goes over is the disulfide.<sup>466e</sup> On vacuum distillation methyl pentasulfide gives the trisulfide<sup>778a</sup> and ethyl pentasulfide, the disulfide.<sup>435a</sup> In the aliphatic series the stability increases with the length of the alkyl.<sup>671</sup> *t*-Butyl trisulfide is exceptionally stable. It is the only polysulfide, so far found, that does not give up sulfur to sodium plumbite.<sup>79</sup>

Ethyl tetrasulfide converts metals to sulfides and potassium cyanide to thiocyanate. Boiling it with aqueous 10% sodium hydroxide takes off sulfur down to the disulfide.<sup>435a</sup> Hydrazine, ethylene diamine, and ammonia do the same.<sup>540c</sup> Sodium sulfide and sulfite solutions will usually strip alkyl polysulfides down to the disulfides. A colorless solution of sodium sulfide becomes colored when shaken with an alkyl tetrasulfide. Sodium arsenite

robs methyl trisulfide of sulfur.<sup>331</sup> Treatment with acetone causes a part of the sulfur of propyl tetrasulfide to separate.<sup>727c</sup> Much sulfur is removed from *o*-nitrophenyl polysulfides by extraction with carbon disulfide.<sup>374</sup> A violent reaction takes place soon after an alkyl polysulfide and powdered silver nitrate are mixed.<sup>655</sup>

Ethyl tetrasulfide is converted to thiophene when it is passed over alumina at a high temperature.<sup>103</sup> Curiously enough a balanced equation can be written but it has no significance:



At 200° phenyl tetrasulfide dehydrogenates tetralin.<sup>839</sup> Aryl polysulfides are taken down to thiophenols by hydrocarbons at 270° or above.<sup>304</sup> Alkyl tetrasulfides are excellent sulfur donors for the sulfuration of organic compounds.<sup>286, 412</sup> In the vulcanization of rubber the replacement of sulfur by certain aryl tetrasulfides has been claimed.<sup>84</sup>

Chlorinating 4-hydroxy- $\alpha$ -naphthyl trisulfide removes all of the sulfur leaving 2,4-dichloro- $\alpha$ -naphthol.<sup>652</sup>

Alkyl polysulfides, containing more than two atoms of sulfur per molecule, are removed from hydrocarbons by treatment with a solution of sodium stannite.<sup>26</sup>

#### APPLICATIONS

A terpene polysulfide has been claimed as a plasticizer for sulfur.<sup>643</sup> Rubber and rubber substitutes are softened by incorporating certain polysulfides.<sup>323</sup> Others may have the same effect on plastics.<sup>836</sup> Still others are recommended for asphalt.<sup>344</sup>

Amyl trisulfide is said to inhibit the oxidation of lubricating oils<sup>683</sup> and diminish corrosion.<sup>759b</sup> *t*-Butyl and *t*-amyl trisulfides are stabilizers for polysulfone resins.<sup>172</sup> Other polysulfides are recommended as additions to lubricating oils,<sup>37, 117a, 132, 759b</sup> especially to those for hypoid gears.<sup>500, 781</sup> Polysulfides, polyselenides, and polytellurides are said to be useful in lubricants.<sup>759a</sup> Methyl, ethyl, propyl, and butyl polysulfides are claimed as improvers for Diesel fuels.<sup>356, 796</sup>

*t*-Butyl trisulfide controls the emulsion polymerization of butadiene and other unsaturated monomers.<sup>171</sup> Trithiodilactic acid is stabilized by thiolactic.<sup>518</sup>

The dimethiodide of *p,p'*-dimethylamindiphenyl disulfide forms a yellow complex with lead ions which may be used for the colorimetric estimation of lead.<sup>721</sup> Many uses for polysulfides have been suggested.<sup>659</sup>

Tetrathiodilactic acid, from thiolactic acid and sulfur chloride, is said to be good for the treatment of rheumatoid arthritis.<sup>479a</sup> The benzyl esters of this acid and of tetrathiodiacetic are recommended for the treatment of skin diseases.<sup>479b</sup> Benzyl tetrasulfide serves the same purpose.<sup>187</sup>

As will be seen in Volume V, polymeric polysulfides have found wide applications, particularly in thioelastomers.

## Physical Properties

### GENERAL

On account of the difficulty of purifying disulfides, the data for them are less accurate than those for the sulfides. The same can be said with greater emphasis about the data for trisulfides and tetrasulfides. The tables, at least, serve the purpose of showing what has been done and by whom. Reference should be made to a review on the properties, characteristics, and toxicology of alkyl disulfides.<sup>158</sup>

There have been numerous studies of the Raman spectra of alkyl disulfides comparing their spectra with those of analogous compounds.<sup>97, 199, 300, 313.5 525, 600, 817, 818, 823</sup> Methyl and ethyl trisulfides have been included in these.<sup>97, 199, 525, 600, 823</sup> Absorption spectra, both infrared<sup>108, 173, 221, 257, 616, 715, 732, 733, 811</sup> and ultraviolet,<sup>34, 108, 302, 440, 478, 540a, 544</sup> have been studied extensively. Absorption by ethyl disulfide begins at around 250  $\mu$  and rises towards 200.<sup>543</sup> *t*-Butyl disulfide does not show a characteristic band at 250.<sup>42.5</sup> It appears that rotation around the S—S bond is restricted and that dimethyl disulfide, MeS·SMe, exists in *cis* and *trans* forms. One author believes that equal amounts of these are present<sup>817</sup> while another finds more of the *cis*, even at elevated temperatures.<sup>300</sup>

The vapor pressure of butyl disulfide has been determined from 10° to 80°.<sup>48</sup> The latent heats of vaporization of methyl and phenyl disulfides have been measured.<sup>599</sup> The heats of formation and free energies of —S·S— groups have been predicted.<sup>258</sup>

The heats of formation of methyl and ethyl disulfides have been calculated from calorimetric data.<sup>259</sup> Specific heats, entropies, and free energies of several disulfides have been determined.<sup>45, 393</sup> The electric moments of *n*-butyl, *i*-butyl, and *t*-butyl disulfides have been compared.<sup>678</sup> The dipole moments of methyl,<sup>456</sup> ethyl,<sup>456, 544</sup> and propyl disulfides and methyl trisulfide have been measured.<sup>456</sup> The value for phenyl disulfide is 1.90 and for the *p*-nitro derivative 4.31.<sup>327</sup>

The valence angle of bivalent sulfur in *p*-bromophenyl disulfide is 107°. <sup>809</sup> The S—S bond distance in  $\beta,\beta'$ -diiododiethyl trisulfide is 2.04 Å and the S—S—S angle is 113°. <sup>183, 197</sup> In dimethyl trisulfide the S—S bond distance is the same but the S—S—S angle is 104°, <sup>198</sup> another value is 107°. <sup>766</sup> In diphenyl diselenide the Se—Se distance is 2.29 Å and the Se—C 1.94 Å. <sup>516</sup>

The diamagnetic susceptibilities of alkyl disulfides show that they have the structure RS·SR and not R<sub>2</sub>S:S. <sup>160</sup> The diamagnetism of butyl mono-, di-, tri-, and tetrasulfides has been studied. <sup>231</sup> Solutions of thiols and of disulfides in concentrated sulfuric acid are strongly colored and show paramagnetic resonance absorptions. Certain similarities of the colors and of the absorptions of all the compounds have been noted. <sup>367.5</sup>

The formation of mixed crystals in binary systems of aryl disulfides and diselenides has been studied. <sup>614, 661, 663, 664, 755a, 756</sup>

The optical activities of *act*-amyl alcohol, mercaptan, sulfide, and disulfide have been compared. The rotations are -4.35°, +2.20°, +24.52°, and +72.48°. <sup>115</sup>

The refractivity of S<sub>2</sub> in a number of disulfides was found to be  $2 \times 7.92$ . <sup>186</sup> The average for four alkyl disulfides was found by another investigator to be 16.07. <sup>821</sup>

Molecular volumes and parachors have been considered with reference to structure. <sup>74, 301</sup> Parachors and surface tensions have been determined for several substituted phenyl disulfides <sup>74</sup> and for a number of aliphatic. <sup>824</sup> The values of the parachors of a number of aryl disulfides agree with the structure ArS·SAr. <sup>73</sup> Several regularities have been found between vapor pressure-temperature relationships and structure. <sup>844</sup>

The refractivity of S<sub>2</sub> in a xanthate is 18.78, of S<sub>3</sub> in a trithiocarbonate 28.02 and of S<sub>4</sub> in an alkyl tetrasulfide 34.91. <sup>101</sup>

Azeotropes with hydrocarbons have been investigated. <sup>192</sup> Data are in Table 2.7.

Special attention is directed to comprehensive studies of the thermodynamic properties of methyl<sup>722</sup> and ethyl<sup>723</sup> disulfides.<sup>336.5</sup>

TABLE 2.7

*Azeotropes of Alkyl Disulfides with Hydrocarbons*<sup>192</sup>

	B.p. Hydrocarbon °C	B.p. Azeotrope °C	Mole % R <sub>2</sub> S <sub>2</sub>
MeS·SMe b. 109.4°			
Hexane	98.5°	96.4°	27.5
Methylcyclohexane	101.0°	98.9°	29.3
2,5-Dimethylhexane	109.1°	102.8°	53.2
2-Methylheptane	117.7°	106.2°	73.3
EtS·SEt b. 154.1°			
Nonane	150.6°	148.6°	42.3
3-Methyl-3-ethylheptane	163.0°	153.0°	82.5

**Symmetrical Aliphatic Disulfides**

Me<sub>2</sub>S<sub>2</sub>, m. -84.72°, <sup>336.5</sup>, <sup>722</sup> -89.69°; <sup>500</sup> b. 109.75°, <sup>722</sup> 109.6°, <sup>336.5</sup> 109.44°, <sup>192</sup> 110°, <sup>83</sup>, <sup>113.5</sup>, <sup>186</sup>, <sup>500</sup> 108.5-9.5°, <sup>179</sup> 114°, <sup>599</sup> 116-8°, <sup>128</sup> 118°; <sup>674</sup> b<sub>744</sub> 112.1°, <sup>613</sup> b<sub>748</sub> 108-8.5°, <sup>394</sup> b<sub>747</sub> 108°, <sup>854</sup> b<sub>774</sub> 109.5°, <sup>822</sup> b<sub>18</sub> 39-41°, <sup>29</sup> b<sub>12</sub> 40°, <sup>446</sup> b<sub>121</sub> 55°; <sup>630a</sup> d<sub>0</sub> 1.06358, <sup>613</sup> d<sub>16</sub> 1.05665, <sup>186</sup> d 16/4 1.0606, <sup>394</sup> d<sub>18</sub> 1.046, <sup>128</sup> d 20/4 1.0647, <sup>822</sup> 1.0625, <sup>336.5</sup> 1.0623, <sup>192</sup>, <sup>500</sup> d 25/4 1.0570, <sup>500</sup> 1.0569, d 30/4 1.05138; <sup>336.5</sup> n 16/D 1.52192, <sup>186</sup> n 20/D 1.52599, <sup>822</sup> 1.5259, <sup>192</sup>, <sup>500</sup> 1.52592, n 25/D 1.52298, <sup>336.5</sup> 1.5227, <sup>500</sup> 1.5221, <sup>854</sup> n 30/D 1.51998; <sup>336.5</sup> heat of vaporization 75 cal./mole; <sup>722</sup> viscosity 0.619 at 20°, 0.585 at 25°, 0.555 at 30°; <sup>336.5</sup> surface tension 34.87 at 14.1°, <sup>822</sup> 33.6 at 20°, 32.8 at 25°, 32.2 at 30°; <sup>336.5</sup> parachor 213.9, <sup>822</sup>

Et<sub>2</sub>S<sub>2</sub>, m. -101.42°, <sup>723</sup> -101.46°, <sup>500</sup> -101.52°; <sup>336.5</sup> b. 153.5°, <sup>674</sup> 152.8°, <sup>236</sup> 152.6°, <sup>336.5</sup> 151°, <sup>170</sup>, <sup>247</sup>, <sup>551</sup> 149.5-50.5°, <sup>813</sup> 154.11°, <sup>192</sup> 150°, <sup>361</sup>, <sup>459</sup> 152.8-3.4°, <sup>573</sup> 152.5-4.0°, <sup>842</sup> 151-2°, <sup>424</sup> 152-4°, <sup>71</sup> 151-4°, <sup>412</sup> 150-1°, <sup>597b</sup>, <sup>626</sup> 154°, <sup>186</sup>, <sup>500</sup> 150-4°, <sup>380b</sup> 150-3°, <sup>395c</sup> 148-50°, <sup>628</sup> b<sub>754</sub> 152°, <sup>822</sup> b<sub>748</sub> 150-1°, <sup>854</sup> b<sub>745</sub> 151.5-3°, <sup>576</sup> b<sub>725</sub> 151-2.5°, <sup>544</sup> b<sub>736</sub> 151-2°, <sup>394</sup> b<sub>10</sub> 39.8-40.8°, <sup>532</sup> 47.5-8.0°, <sup>328</sup> b<sub>11</sub> 46°, <sup>113.7</sup>, <sup>241</sup> b<sub>12</sub> 65°, <sup>446</sup> b<sub>15</sub> 35-41°, <sup>87</sup> b<sub>121</sub> 93°; <sup>630a</sup> d<sub>19.5</sub> 1.199, <sup>241</sup>

- d 20/4 0.9933,<sup>192, 500</sup> 0.99311,<sup>336.5</sup> 0.9927,<sup>71</sup> 0.99267,<sup>186, 573</sup> 0.9926,<sup>44</sup> 0.9920,<sup>822</sup> 0.9961,<sup>394</sup> 0.9982,<sup>576</sup> d 25/4 0.9882,<sup>500</sup> 0.98818, d 30/4 0.98332;<sup>336.5</sup> n 20/D 1.50687,<sup>328</sup> 1.5070,<sup>71</sup> 1.50704,<sup>822</sup> 1.5072,<sup>192, 500</sup> 1.50731,<sup>336.5</sup> 1.5078,<sup>87, 842</sup> 1.50633,<sup>186, 573</sup> 1.5030,<sup>576</sup> n 25/D 1.5046,<sup>500</sup> 1.50470, n 30/D 1.50198;<sup>336.5</sup> critical temperature 368.93°;<sup>236</sup> dipole moment 1.99  $\times 10^{-10}$ ;<sup>842</sup> dielectric constant 15.6 at 19.0°;<sup>213</sup> diamagnetic susceptibility 83.63;<sup>160</sup> viscosity 0.860 at 20°, 0.805 at 25°, 0.757 at 30°; surface tension 31.3 at 20°, 30.7 at 25°, 30.2 at 30°;<sup>336.5</sup> 31.19 at 173°; parachor 291.1;<sup>822</sup> 287.6.<sup>44</sup>
- $\text{Pr}_2\text{S}_2$ , m. -85.59°;<sup>500</sup> b. 194°,<sup>129</sup> 195°,<sup>500</sup> 195-6°,<sup>29</sup> 192.5°,<sup>757</sup> 190-4°,<sup>109</sup> 191-2°,<sup>71</sup> b<sub>750</sub> 193.5°; d 20/4 0.9599,<sup>822</sup> 0.9596,<sup>500</sup> 0.9525,<sup>71</sup> d 25/4 0.9549;<sup>500</sup> n 20/D 1.49813,<sup>822</sup> 1.4980,<sup>500</sup> 1.4981,<sup>71</sup> n 25/D 1.4954,<sup>500</sup> 1.4961;<sup>129</sup> diamagnetic susceptibility 106.23;<sup>160</sup> surface tension 30.68 at 18.8°; parachor 368.5.<sup>822</sup>
- i*- $\text{Pr}_2\text{S}_2$ , m. -69.08°;<sup>500</sup> b<sub>7.5</sub> 54-5°;<sup>854</sup> b<sub>71</sub> 97-8°, b<sub>760</sub> 176°,<sup>159</sup> b<sub>767</sub> 176°;<sup>822</sup> b. 174°,<sup>81a, 500</sup> 174.5°,<sup>537, 757</sup> 175-7°;<sup>109</sup> d 20/4 0.9427,<sup>500</sup> 0.9435,<sup>822</sup> d 25/4 0.9381,<sup>500</sup> d 25/4 1.0829;<sup>854</sup> n 20/D 1.4917,<sup>500</sup> 1.49164,<sup>822</sup> 1.4948,<sup>854</sup> n 25/D 1.4891;<sup>129, 500</sup> surface tension 28.60 at 18.4°; parachor 368.0.<sup>822</sup>
- $\text{Bu}_2\text{S}_2$ , b. 226°;<sup>782</sup> b<sub>755</sub> 230.5°;<sup>822</sup> b<sub>740</sub> 226-9°, b<sub>735</sub> 227-9°;<sup>394</sup> b<sub>3</sub> 85°;<sup>79</sup> 90-100°;<sup>841</sup> b<sub>4</sub> 88°;<sup>81b</sup> b<sub>9</sub> 102-4°;<sup>201</sup> b<sub>10</sub> 102.0-2.4°;<sup>21</sup> b<sub>15</sub> 110-2°;<sup>732</sup> 110-5°;<sup>651</sup> 110-3°;<sup>309</sup> b<sub>17</sub> 115°;<sup>678</sup> b<sub>20</sub> 116-8°;<sup>436b</sup> b<sub>83</sub> 143-4°;<sup>71</sup> vapor pressure 10° 0.4 mm., 20° 0.6, 30° 0.9, 40° 1.3, 50° 1.7, 60° 2.2, 70° 2.9, 80° 4.0;<sup>48</sup> d<sub>20</sub> 0.9371,<sup>79</sup> d 20/4 0.928,<sup>574</sup> 0.9383,<sup>822</sup> 0.9306,<sup>71</sup> 0.930,<sup>309</sup> 0.942,<sup>782</sup> d<sub>25</sub> 0.9231,<sup>79</sup> d 25/4 0.93245,<sup>678</sup> 0.9327;<sup>394</sup> n 20/D 1.4923,<sup>29</sup> 1.49259,<sup>822</sup> 1.4926,<sup>782</sup> 1.49208,<sup>71</sup> 1.4982,<sup>201</sup> 1.494,<sup>309</sup> n 25/D 1.4905;<sup>678</sup> surface tension 31.01 at 15.5°; parachor 447.7.<sup>822</sup>
- i*- $\text{Bu}_2\text{S}_2$ , b. 220°;<sup>757</sup> 215°;<sup>81a</sup> b<sub>767</sub> 215°;<sup>822</sup> b<sub>3</sub> 84°;<sup>30</sup> b<sub>17</sub> 97.0°;<sup>678</sup> d 20/4 0.9275,<sup>822</sup> 0.928,<sup>574</sup> d 25/4 0.92225;<sup>678</sup> n 20/D 1.4867,<sup>574</sup> 1.48666,<sup>822</sup> n 25/D 1.4847;<sup>678</sup> surface tension 28.29 at 17.1°; parachor 443.4.<sup>822</sup>
- s*- $\text{Bu}_2\text{S}_2$ , b<sub>14</sub> 95-7°; d 14/4 0.942; n 18.5/D 1.5031; [ $\alpha$ ] 14/5893 -93.55°, [ $\alpha$ ] 14/425.9 196.9°, [ $\alpha$ ] 5461 -111.25°.<sup>425</sup>
- t*- $\text{Bu}_2\text{S}_2$ , m. -4.95°;<sup>79</sup> b. 200-1°, b<sub>4</sub> 64-5°;<sup>29</sup> b<sub>5.5</sub> 64°;<sup>822</sup> b<sub>10</sub> 73-5°;<sup>30</sup> b<sub>11</sub> 72°;<sup>665, 678</sup> b<sub>16</sub> 78-80°;<sup>732</sup> 79-80°;<sup>575</sup> b<sub>17</sub> 81-2°;<sup>29</sup> b<sub>20</sub> 84-5°;<sup>665</sup> b<sub>21</sub> 88°;<sup>29</sup> b<sub>25</sub> 85°;<sup>42.5</sup> d<sub>20</sub> 0.9226,<sup>79</sup> d 20/4 0.9229,<sup>822</sup> d 25/4 0.9194;<sup>678</sup> n 15/D 1.4912,<sup>29</sup> n 17/D 1.4928,<sup>575</sup> n 20/D

- 1.49003,<sup>822</sup> 1.4899,<sup>79</sup> 1.4921;<sup>30</sup> surface tension 27.32 at 17.5°; parachor 440.9;<sup>822</sup> heat fusion 3.144 k. cal./mole.<sup>79</sup>
- $\text{Am}_2\text{S}_2$ ,  $b_1$  74–5°;<sup>689</sup> 90–2°, 89–91°;<sup>537</sup>  $b_{2.5}$  105–7°;<sup>689</sup>  $b_7$  119°;<sup>822</sup>  $b_{17}$  140.5–2°;<sup>83</sup>  $d$  20/4 0.9221,<sup>822</sup>  $d$  25/4 0.9197;<sup>537</sup>  $n$  20/D 1.48887,<sup>822</sup> 1.4876,<sup>537</sup>  $n$  24.5/D 1.4867,<sup>689</sup>  $n$  25/D 1.4875;<sup>537</sup> surface tension 29.72 at 18.5°; parachor 524.6.<sup>822</sup>
- i*- $\text{Am}_2\text{S}_2$ ,  $b$ . 250°;<sup>757</sup> 240–60°;<sup>362</sup>  $b_9$  115°;<sup>822</sup>  $b_{12}$  123.5–4°;<sup>394</sup>  $d_{13}$  0.880,<sup>330</sup>  $d_{18}$  0.918,<sup>362</sup>  $d$  18/4 0.9188,<sup>391</sup>  $d$  20/4 0.9192;  $n$  20/D 1.48637; surface tension 29.08 at 13.4°; parachor 521.2.<sup>822</sup>
- act*- $\text{Am}_2\text{S}_2$ ,  $b_{10}$  122–3°;  $d$  20/4 0.923;  $[\alpha]$  20/D 72.48°.<sup>115</sup>
- t*- $\text{Am}_2\text{S}_2$ ,  $b_5$  98°;  $d_{20}$  0.9342,  $d_{25}$  0.9304;  $n$  20/D 1.4988,  $n$  25/D 1.4965.<sup>79</sup>
- n*-Heptyl $_2\text{S}_2$ ,  $b_5$  143–7°;<sup>841</sup>  $b_6$  164°;  $d$  15.5/4 0.9073.<sup>81b</sup>
- 3-Heptyl $_2\text{S}_2$ ,  $b_3$  130–1°;  $d$  20/4 0.9033;  $n$  20/D 1.4865.<sup>530</sup>
- (*i*-AmPrCH) $_2\text{S}_2$ ,  $b_7$  165–7°;  $d$  20/4 0.8925;  $n$  20/D 1.4819.<sup>530</sup>
- (*i*-Am-*i*-PrCH) $_2\text{S}_2$ ,  $b_1$  148–56°;  $d$  20/4 0.9128;  $n$  20/D 1.4923.<sup>530</sup>
- Oct $_2\text{S}_2$ ,  $b_{1.5}$  160–3°;<sup>508</sup>  $b_5$  178–83°.<sup>841</sup>
- i*-Oct $_2\text{S}_2$ ,  $d$  20/4 0.86;  $n$  20/D 1.4815.<sup>71</sup>
- s*-Oct $_2\text{S}_2$ ,  $b_6$  169–71°;  $d$  20/4 0.9010;  $n$  20/D 1.4871.<sup>530</sup>
- (PrBuCH) $_2\text{S}_2$ ,  $b_1$  137–9°;  $d$  20/4 0.9003;  $n$  20/D 1.4857.<sup>530</sup>
- (*i*-PrBuCH) $_2\text{S}_2$ ,  $b_1$  137–8°;  $d$  20/4 0.9147;  $n$  20/D 1.4880.<sup>530</sup>
- t*-Oct $_2\text{S}_2$ ,  $d_{25}$  0.9152;  $n$  20/D 1.4998.<sup>718c</sup>
- Non $_2\text{S}_2$ ,  $b_6$  211–2°;<sup>805</sup>  $b_7$  185–93;  $d$  20/4 0.8772,<sup>530</sup> 0.8922;  $n$  20/D 1.4382;<sup>805</sup> 1.4775.<sup>530</sup>
- 3-Non $_2\text{S}_2$ ,  $b_2$  155°;  $d$  20/4 0.8933;  $n$  20/D 1.4819.<sup>530</sup>
- (*i*-AmPrCH) $_2\text{S}_2$ ,  $b_7$  165–7°;  $d$  20/4 0.8925;  $n$  20/D 1.4819.<sup>530</sup>
- (*i*-Am-*i*-PrCH) $_2\text{S}_2$ ,  $b_1$  148–56°;  $d$  20/4 0.9128;  $n$  20/D 1.4923.<sup>530</sup>
- (Bu $_2$ CH) $_2\text{S}_2$ ,  $b_6$  175–85°;  $d$  20/4 0.8936;  $n$  20/D 1.4841.<sup>530</sup>
- (*i*-Bu $_2$ CH) $_2\text{S}_2$ ,  $b_1$  150°;  $d$  20/4 0.8870;  $n$  20/D 1.4795.<sup>530</sup>
- (*i*-BuBuCH) $_2\text{S}_2$ ,  $b_1$  143–51°;  $d$  20/4 0.9040;  $n$  20/D 1.4820.<sup>530</sup>
- (Me $_3$ CCH $_2$ CHMeCH $_2$ CH $_2$ ) $_2\text{S}_2$ ,  $b_{0.4}$  128–9°;  $d$  20/4 0.901;  $n$  25/D 1.4803.<sup>129</sup>
- Dec $_2\text{S}_2$ ,  $b_2$  206–7°,  $b_7$  210–2;  $d$  20/4 0.8894,<sup>805</sup> 0.8907;  $n$  20/D 1.4813,<sup>530</sup> 1.4818.<sup>805</sup>
- 4-Dec $_2\text{S}_2$ ,  $d$  20/4 0.8946;  $n$  20/D 1.4815.<sup>530</sup>
- (*i*-Bu-*i*-AmCH) $_2\text{S}_2$ ,  $b_3$  145–50°;  $d$  20/4 0.8909;  $n$  20/D 1.4765.<sup>530</sup>
- (MeBu $_2$ C) $_2\text{S}_2$ ,  $d$  20/4 0.9135;  $n$  20/D 1.487.<sup>530</sup>
- (BuHexCH) $_2\text{S}_2$ ,  $b_1$  190–2°;  $d$  20/4 0.8840;  $n$  20/D 1.4811.<sup>530</sup>
- (*i*-BuHexCH) $_2\text{S}_2$ ,  $b_1$  175–80°;  $d$  20/4 0.8905;  $n$  20/D 1.4820.<sup>530</sup>
- (*i*-Am $_2$ CH) $_2\text{S}_2$ ,  $d$  20/4 0.8873;  $n$  20/D 1.4821.<sup>530</sup>



- Dodec<sub>2</sub>S<sub>2</sub>, m. 34.5°, <sup>651</sup> 34°, <sup>251, 841</sup> 32°, <sup>168</sup> 31°. <sup>72</sup>  
 Tridec<sub>2</sub>S<sub>2</sub>, m. 44°. <sup>251</sup>  
 Tetradec<sub>2</sub>S<sub>2</sub>, m. 46°. <sup>251</sup>  
 Cetyl<sub>2</sub>S<sub>2</sub>, m. 55.5°, <sup>34, 855</sup> 54°, <sup>168, 251</sup> 52°, <sup>72</sup> 50.5°, <sup>262</sup> 50°; <sup>246</sup> dipole moment 2.00. <sup>855</sup>  
 Heptadec<sub>2</sub>S<sub>2</sub>, m. 60°. <sup>251</sup>  
 Octadec<sub>2</sub>S<sub>2</sub>, m. 62.5°, <sup>168, 251</sup> 56°. <sup>841</sup>  
 Nonadec<sub>2</sub>S<sub>2</sub>, m. 69°. <sup>251</sup>  
 Allyl<sub>2</sub>S<sub>2</sub>, b. 174° with decomposition, b<sub>48</sub> 100°, <sup>85b</sup> b<sub>16</sub> 78–80°, <sup>728</sup> b<sub>13.8</sub> 74.8°; d 25/4 0.9919, <sup>726</sup> d<sub>14.8</sub> 1.0237, <sup>728</sup> d<sub>15</sub> 1.010; <sup>85b</sup> n 25/D 1.5312. <sup>726</sup>  
 (MeHC:CMech<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, b<sub>1</sub> 55–60°; d 26/4 0.975; n 20/D 1.530. <sup>18</sup>  
 (PrCH:CMechPr)<sub>2</sub>S<sub>2</sub>, n 20/D 1.502. <sup>18</sup>  
 (PhCH:CHCH<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, m. 90–5°, <sup>493</sup> 89°. <sup>77</sup>

### Cyclic Disulfides

- Cyclopentyl<sub>2</sub>S<sub>2</sub>, b<sub>1.5</sub> 105.5–6°, b<sub>2</sub> 110.5°, <sup>812a</sup> b<sub>5</sub> 130.5–1.0°; d 20/4 1.0617; n 20/D 1.5478, <sup>804b</sup> 1.5361. <sup>812a</sup>  
 Cyclohexyl<sub>2</sub>S<sub>2</sub>, b. 288°, <sup>510</sup> b<sub>0.001</sub> 100°, <sup>87</sup> b<sub>0.01</sub> 100°, <sup>732</sup> b<sub>0.1</sub> 106°, <sup>229</sup> b<sub>0.2</sub> 110–2°, <sup>575</sup> b<sub>0.25</sub> 130–1°, <sup>835a</sup> b<sub>0.7</sub> 110°, <sup>129</sup> b<sub>1</sub> 130°, <sup>835b</sup> b<sub>1.5</sub> 128–9°, <sup>812a</sup> b<sub>7</sub> 166–7°, <sup>804b</sup> b<sub>15</sub> 120–2°, <sup>864</sup> b<sub>14</sub> 125°; <sup>760b</sup> d<sub>20</sub> 1.0457, <sup>835a</sup> d 20/4 1.0489; <sup>804b</sup> n 20/D 1.5450 <sup>812a</sup> 1.5454, <sup>835a</sup> 1.5462, <sup>87</sup> 1.5482, <sup>804b</sup> n 25/D 1.5462. <sup>129</sup>  
 2-Mecyclohexyl<sub>2</sub>S<sub>2</sub>, *trans* b<sub>15</sub> 100–10°. <sup>864</sup>  
 3-Mecyclohexyl<sub>2</sub>S<sub>2</sub>, b<sub>20</sub> 198°; d<sub>25</sub> 0.9480; n 25/D 1.5050. <sup>557, 558</sup>  
 2,2,6,6-Tetramethylcyclohexyl<sub>2</sub>S<sub>2</sub>, m. 59.5°. <sup>457</sup>  
 Ph<sub>2</sub>S<sub>2</sub>, m. 66.5°, <sup>73</sup> 62°, <sup>44, 466a, 469</sup> 61.5°, <sup>380b</sup> 61°, <sup>131, 392, 526, 597a, 599, 638, 662a, 684, 741.5, 778b, 859</sup> 60.5°, <sup>244.5, 245</sup> 60.3°, <sup>327</sup> 60°, <sup>202, 312, 449, 451, 787a, 787d, 825</sup> 59°, <sup>182</sup> 53–6°; <sup>791</sup> b. 310°, <sup>14, 317</sup> b<sub>8</sub> 160–9°, <sup>526</sup> b<sub>13</sub> 187–9°, <sup>449</sup> b<sub>14</sub> 175–95°, <sup>684</sup> b<sub>15</sub> 190–2°; <sup>14, 451</sup> d 20/4 1.353, <sup>44</sup> d 118/4 1.110; <sup>73</sup> dipole moment 1.90; <sup>327</sup> surface tension 39.03 at 79.1°, 37.29 at 96.8°; parachor 477.6, <sup>74</sup> 477.9. <sup>73</sup>  
 (*o*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>2</sub>, m. 39°, <sup>787d</sup> 38°. <sup>167</sup>  
 (*m*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>2</sub>, m. –21°, <sup>167</sup> –22°. <sup>391</sup>  
 (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>2</sub>, m. 48°, <sup>741</sup> 47°, <sup>63</sup> 46°, <sup>73, 167, 182, 244.5, 380c, 434, 476, 576, 684, 787d, 866</sup> 45.8°, <sup>327</sup> 45.5°, <sup>245, 307</sup> 45.2°; <sup>390</sup> b<sub>20</sub> 210–5°; <sup>741</sup> d 111/4 1.068; parachor 552.9, <sup>73</sup> 552.5. <sup>74</sup>  
 (*p-t*-BuC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>2</sub>, m. 89°. <sup>30</sup>  
 (2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>S<sub>2</sub>, m. 47°. <sup>787d</sup>  
 (2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, m. 125°. <sup>30</sup>  
 (PhCH<sub>2</sub>)<sub>2</sub>, m. 74°, <sup>67.5</sup> 72°, <sup>780</sup> 71.5°, <sup>394, 506</sup> 71°, <sup>73, 749, 791</sup> 70°. <sup>278</sup>

- 67.5°,<sup>591</sup> 68°,<sup>129</sup>  $\alpha$ - m. 62°,  $\beta$ - m. 70°; <sup>367c</sup> d 100/4 1.085; parachor 557.1,<sup>73</sup> 556.7.<sup>74</sup>
- (PhCHMe)<sub>2</sub>S<sub>2</sub> m. 58°,<sup>51</sup> 381a 56°.<sup>381c</sup>
- (Ph<sub>2</sub>CH)<sub>2</sub>S<sub>2</sub>, m. 153°,<sup>1</sup> 152°.<sup>75b</sup>, 760a
- (Ph<sub>3</sub>C)<sub>2</sub>S<sub>2</sub>, m. circa 155°.<sup>826a</sup>
- (PhCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, b<sub>0.8</sub> 172–5°, b<sub>1.5</sub> 168–80°.<sup>506</sup>
- (PhCH<sub>2</sub>CHMe)<sub>2</sub>S<sub>2</sub>, b<sub>0.1</sub> 144°; d 20/4 1.072; n 24.5/D 1.5794.<sup>425</sup>
- [Ph(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>S<sub>2</sub>, b<sub>0.03–0.04</sub> 165–6°; n 20/D 1.5877.<sup>812b</sup>
- [Ph(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>]<sub>2</sub>S<sub>2</sub>, b<sub>0.2</sub> 195°; n 20/D 1.5750.<sup>812b</sup>
- [Ph(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>]<sub>2</sub>S<sub>2</sub>, m. 24°.<sup>812b</sup>
- (MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, ortho, m. 85°; para, m. 43°.<sup>780</sup>
- (*p*-PhC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>2</sub>, m. 150°,<sup>289</sup> 50°.<sup>787d</sup>
- ( $\alpha$ -C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>S<sub>2</sub>, m. 91°,<sup>476</sup> 86°,<sup>787d</sup> 85°; <sup>695</sup>, <sup>787a</sup> b<sub>15</sub> 290°.<sup>448</sup>, <sup>450</sup>
- ( $\beta$ -C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>S<sub>2</sub>, m. 139°,<sup>53</sup>, <sup>73</sup>, <sup>157</sup>, <sup>469</sup>, <sup>741.5</sup> 137°; <sup>476</sup> b<sub>15</sub> 295–6°; <sup>14</sup> d 144/4 1.144; parachor 689.6,<sup>73</sup> 689.5.<sup>74</sup>
- ( $\beta$ -C<sub>10</sub>H<sub>17</sub>)<sub>2</sub>S<sub>2</sub>, decahydronaphthyl, b<sub>20</sub> 230°; d<sub>25</sub> 1.022; n 25/D 1.5437.<sup>557</sup>
- (2-C<sub>4</sub>H<sub>3</sub>O·CH<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, b<sub>5</sub> 160–5°.<sup>306</sup>
- (2-C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub>S<sub>2</sub>, m. 56°.<sup>127</sup>, <sup>143</sup>, <sup>534</sup>
- (C<sub>10</sub>H<sub>17</sub>)<sub>2</sub>S<sub>2</sub>, (thiobornyl), m. 121°,<sup>98</sup> 178°.<sup>389</sup>

### Hydroxy-, Alkoxy-, Aldo-, and Keto Disulfides

- (HOCHPh)<sub>2</sub>S<sub>2</sub>, m. 65°.<sup>78</sup>
- (HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, m. 28°,<sup>436b</sup> 26°; b<sub>0.015</sub> 106°,<sup>295</sup> b<sub>0.8</sub> 141–3°; <sup>436b</sup> di-*p*-nitrobenzoate, m. 145°.<sup>65</sup>
- (HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, b<sub>0.8</sub> 160°,<sup>739</sup> b<sub>0.5</sub> 136–40°; di-3,5-dinitrobenzoate, m. 140°.<sup>159</sup>
- (HOCH<sub>2</sub>CH<sub>2</sub>CHMe)<sub>2</sub>S<sub>2</sub>, diAc., b<sub>3</sub> 158°.<sup>121</sup>
- [C<sub>6</sub>H<sub>8</sub>(OH)<sub>5</sub>]<sub>2</sub>S<sub>2</sub>, (from thiosorbitol), m. 128°,<sup>463</sup> 128–30°.<sup>228</sup>
- (*m*-HOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>2</sub>, m. 95°,<sup>870a</sup> 90°.<sup>833</sup>
- (*p*-HOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>S<sub>2</sub>, m. 152°,<sup>508</sup> 151°; <sup>476</sup>, <sup>850</sup> diAc., m. 91°,<sup>508</sup> 89°; <sup>476</sup>, <sup>870b</sup> Ac.-Bz., m. 100°; monoBz., m. 130°; diBz., m. 166°.<sup>508</sup>
- (*o*-HOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, m. 103.5°.<sup>512</sup>
- (2-HO- $\alpha$ -C<sub>10</sub>H<sub>6</sub>)<sub>2</sub>S<sub>2</sub>, m. 169°,<sup>593</sup> 166°; <sup>360</sup> diAc., m. 140°; diBz., m. 187°.<sup>593</sup>
- (4-HO- $\alpha$ -C<sub>10</sub>H<sub>6</sub>)<sub>2</sub>S<sub>2</sub>, m. 152°,<sup>878</sup> 212°; <sup>6</sup> diAc., m. 112°.<sup>878</sup>
- (5-HO- $\alpha$ -C<sub>10</sub>H<sub>6</sub>)<sub>2</sub>S<sub>2</sub>, m. 212°,<sup>657</sup> 200°; <sup>833</sup> diAc., m. 154°.<sup>657</sup>
- (6-HO- $\beta$ -C<sub>10</sub>H<sub>6</sub>)<sub>2</sub>S<sub>2</sub>, m. 221°; diAc., m. 168°.<sup>869</sup>
- (MeOCH<sub>2</sub>)<sub>2</sub>S<sub>2</sub>, b<sub>15</sub> 115°; d 0/4 1.2083, d 22/4 1.1855; n 20/D 1.5290.<sup>462</sup>
- [(MeO)<sub>2</sub>CHCH<sub>2</sub>]<sub>2</sub>S<sub>2</sub>, b<sub>0.6</sub> 101°; n 30/D 1.4868.<sup>603</sup>

- $(\text{EtOCH}_2\text{CH}_2)_2\text{S}_2$ ,  $b_{15}$  150–2°, <sup>680</sup>  $b_{33}$  161°;  $d$  20/4 1.0492.<sup>785</sup>  
 $(\text{EtOCHEtCH}_2)_2\text{S}_2$ ,  $b_8$  135°;  $d$  20/4 0.9995.<sup>785</sup>  
 $(\text{PhOCH}_2\text{CH}_2)_2\text{S}_2$ ,  $m$ . 97°, <sup>64</sup> 96°. <sup>429</sup>  
 $(o\text{-MeOC}_6\text{H}_4)_2\text{S}_2$ ,  $m$ . 120°, <sup>296a</sup> 119°. <sup>167</sup>, 337  
 $(m\text{-MeOC}_6\text{H}_4)_2\text{S}_2$ ,  $m$ . 109°. <sup>167</sup>  
 $(p\text{-MeOC}_6\text{H}_4)_2\text{S}_2$ ,  $m$ . 45°, <sup>296a</sup> 44°, <sup>787b</sup> 119°, <sup>167</sup> 73.5°;  $d$  100/4 1.139; parachor 666.1, <sup>73</sup> 665.5. <sup>74</sup>  
 $[2,4\text{-(MeO)}_2\text{C}_6\text{H}_3]_2\text{S}_2$ ,  $m$ . 117°. <sup>125</sup>  
 $[3,4\text{-(MeO)}_2\text{C}_6\text{H}_3]_2\text{S}_2$ ,  $m$ . 89°. <sup>267</sup>  
 $[3,4,5\text{-(MeO)}_2(\text{EtO})\text{C}_6\text{H}_2]_2\text{S}_2$ ,  $m$ . 84°. <sup>267</sup>  
 $[2,5\text{-(MeO)MeC}_6\text{H}_3]_2\text{S}_2$ ,  $m$ . 74°. <sup>364</sup>  
 $[4,3\text{-(MeO)MeC}_6\text{H}_3]_2\text{S}_2$ ,  $m$ . 67°, <sup>767</sup> 64.5°. <sup>296a</sup>  
 $(o\text{-EtOC}_6\text{H}_4)_2\text{S}_2$ ,  $m$ . 90°. <sup>296a</sup>  
 $(m\text{-EtOC}_6\text{H}_4)_2\text{S}_2$ ,  $m$ . 43°. <sup>188</sup>  
 $(p\text{-EtOC}_6\text{H}_4)_2\text{S}_2$ ,  $m$ . 49°, <sup>296a</sup> 48°, <sup>787d</sup> 47°. <sup>787b</sup>  
 $(p\text{-MeOC}_6\text{H}_4\text{CH}_2)_2\text{S}_2$ ,  $m$ . 101°. <sup>512</sup>  
 $(2\text{-EtO-}\alpha\text{-C}_{10}\text{H}_6)_2\text{S}_2$ ,  $m$ . 158.5°. <sup>593</sup>  
 $\left[ \begin{array}{c} \text{CMe}_2\text{O} \\ \diagdown \quad \diagup \\ \text{CHCH}_2 \\ \diagup \quad \diagdown \\ \text{OCH}_2 \end{array} \right]_2\text{S}_2$ ,  $b_3$  165°;  $d$  20/4 1.1455;  $n$  20/D 1.4998. <sup>748</sup>  
 $(\text{OCHCMe}_2)_2\text{S}_2$ ,  $b_1$  100–10°. <sup>580</sup>  
 $(o\text{-OCHCH}_2\text{SC}_6\text{H}_4)_2\text{S}_2$ , 2,4-dinitrophenylhydrazone,  $m$ . 164.5°. <sup>602</sup>  
 $(\text{MeCO})_2\text{CHSSCH}(\text{COMe})_2$ ,  $m$ . 91°, <sup>816</sup> 90°. <sup>507</sup>  
 $(\text{PhCOCH}_2)_2\text{S}_2$ ,  $m$ . 81°. <sup>322</sup>  
 $(\text{MeCOCH}_2\text{CMe}_2)_2\text{S}_2$ ,  $b_{14}$  170–80°. <sup>20</sup>  
 $(p\text{-MeCOC}_6\text{H}_4)_2\text{S}_2$ ,  $m$ . 100°. <sup>363</sup>, 793  
 $[2,5\text{-MeCO}(\text{MeO})\text{C}_6\text{H}_3]_2\text{S}_2$ ,  $m$ . 153°. <sup>793</sup>  
 $[4,3\text{-MeCO}(\text{MeO})\text{C}_6\text{H}_3]_2\text{S}_2$ ,  $m$ . 180°. <sup>363</sup>  
 $[3,4\text{-MeCO}(\text{HO})\text{-}\alpha\text{-C}_{10}\text{H}_5]_2\text{S}_2$ ,  $m$ . 185°. <sup>6</sup>  
 $(\alpha\text{-C}_{14}\text{H}_7\text{O}_2)_2\text{S}_2$ , (anthraquinone),  $m$ . > 350°. <sup>296b</sup>  
 $(\beta\text{-C}_{14}\text{H}_7\text{O}_2)_2\text{S}_2$ ,  $m$ . 257°. <sup>296b</sup>  
 $(\text{XC}_{14}\text{H}_6\text{O}_2)_2\text{S}_2$ . <sup>296b</sup>  
     2-Me-,  $m$ . 247°.                      4- $p\text{-MeC}_6\text{H}_4$ -,  $m$ . > 330°.  
     4-HO-,  $m$ . > 300°.                    3,4-(HO)<sub>2</sub>-,  $m$ . > 300°.  
     4-MeO-,  $m$ . 283°.                      5-Cl-,  $m$ . > 360°.

### Halo-Disulfides

- $(\text{F}_3\text{C})_2\text{S}_2$ ,  $b$ . 34.6°; heat vaporization 6880 cal./mole. <sup>108</sup>  
 $(\text{ClCH}_2)_2\text{S}_2$ ,  $b_6$  75–7°, <sup>200</sup>  $b_{10}$  90°, <sup>114</sup>  $b_{15}$  98.5–9.5°, <sup>180</sup>  $b_{16}$  45–6°,

- $b_{760}$  144–6°;  $^{114.5}$   $d$  0/4 1.495, $^{200}$   $d_{20}$  1.499, $^{114}$   $d$  20/4 1.470; $^{200}$   
 $n$  17/D 1.5894, $^{180}$   $n$  20/D 1.5863. $^{200}$   
 $(Cl_3C)_2S_2$ ,  $b$ . 150–5°, $^{670}$   $b_{10}$  130°. $^{691}$   
 $(ClCHMe)_2S_2$ ,  $b_9$  84°. $^{113.3}$   
 $(ClCH_2CH_2)_2S_2$ ,  $m$ . 1.0°, $^{285}$  0.2°, $^{429}$  0°; $^{295}$   $b$ . 170–80°, $^{169}$   $b_{0.3}$   
 90–2°, $^{429}$   $b_{0.4}$  97–8°, $^{286}$   $b_{0.5}$  100°, $^{295}$   $b_2$  83–8°, $^{285}$   $b_{10}$  124–7°, $^{184}$   
 $b_{30}$  155°, $^{64}$   $b_{40}$  160–5°; $^{611}$   $d$  11/4 1.599,  $d$  19/4 1.344, $^{330}$   $d$  20/4  
 1.3375; $^{64}$ ,  $^{184}$   $n$  20/D 1.5670, $^{285}$  1.5656. $^{286}$   
 $ClCH_2CH_2SSCH_2CHMeCl$ ,  $b_1$  74–4.5°;  $n$  20/D 1.5518. $^{282}$   
 $(ClCHMeCH_2)_2S_2$ ,  $b_{18-25}$  113–20°. $^{165}$   
 $(ClCH_2CHMe)_2S_2$ ,  $b_1$  98–101°;  $n$  20/D 1.5400. $^{769}$   
 $(ClCMe_2CHMe)_2S_2$ ,  $b_{11}$  150–60°. $^{615}$   
 $(BrCH_2CHMe)_2S_2$ ,  $b_1$  114–7°;  $n$  20/D 1.5838. $^{769}$   
 $(ICH_2CH_2)_2S_2$ ,  $m$ . 42°. $^{429}$   
 $(ClCF_2CF_2)_2S_2$ ,  $b$ . 141–2°. $^{637}$   
 $(ClCH_2CH_2CH_2)_2S_2$ ,  $b_1$  113–15°;  $n$  20/D 1.5450. $^{768}$   
 $(ClCH_2CHClCH_2)_2S_2$ ,  $b_{15}$  181°. $^{615}$   
 $(CF_3CF_2CF_2)_2S_2$ ,  $b$ . 122.2°;  $d$  28/4 1.6940;  $n$  28/D 1.3222. $^{353}$   
 $(ClCH_2CH_2CH_2CH_2CH_2CH_2)_2S_2$ ,  $b_{0.3}$  191–4°. $^{824}$   
 $(o-ClC_6H_4)_2S_2$ ,  $m$ . 90°. $^{30}$ ,  $^{265}$   
 $(p-ClC_6H_4)_2S_2$ ,  $m$ . 73°, $^{754}$  71.3°, $^{663}$  71°, $^{787a}$ ,  $^{787d}$  71.5°;  $^{73}$ ,  $^{741.5}$   
 $d$  102/4 1.304; $^{73}$  parachor 550.1, $^{74}$  550.6. $^{73}$   
 $(2,4-Cl_2C_6H_3)_2S_2$ ,  $m$ . 71°, $^{578}$  82.5°, $^{31}$  83°. $^{754}$   
 $(2,5-Cl_2C_6H_3)_2S_2$ ,  $m$ . 83°, $^{298}$  82°. $^{546}$ ,  $^{767}$   
 $(2,4,6-Cl_3C_6H_2)_2S_2$ ,  $m$ . 165°. $^{31}$   
 $(Cl_5C_6)_2S_2$ ,  $m$ . 229°. $^{788.5}$   
 $(3,4-ClMeC_6H_3)_2S_2$ ,  $m$ . 78°. $^{546}$   
 $(5,2-ClMeC_6H_3)_2S_2$ ,  $m$ . 82.7°. $^{16}$   
 $(o-ClC_6H_4CH_2)_2S_2$ ,  $m$ . 90°, $^{149}$  87.5°. $^{755b}$   
 $(p-ClC_6H_4CH_2)_2S_2$ ,  $m$ . 59°. $^{149}$ ,  $^{404}$   
 $(2,4-Cl_2C_6H_3CH_2)_2S_2$ ,  $m$ . 75°. $^{149}$   
 $(3,4-Cl_2C_6H_3CH_2)_2S_2$ ,  $m$ . 95°. $^{149}$   
 $(\alpha-5-ClC_{10}H_6)_2S_2$ ,  $m$ . 170°. $^{654}$   
 $(\alpha-4-ClC_{10}H_6)_2S_2$ ,  $m$ . 122°. $^{787a}$ ,  $^{787d}$   
 $(1,4-HOCl-\beta-C_{10}H_5)_2S_2$ ,  $m$ . 147°;  $diAc.$ ,  $m$ . 148°. $^{303}$   
 $(o-BrC_6H_4)_2S_2$ ,  $m$ . 98°. $^{848}$   
 $(m-BrC_6H_4)_2S_2$ ,  $b_{0.4}$  187–90°. $^{848}$   
 $(p-BrC_6H_4)_2S_2$ ,  $m$ . 94.5°, $^{244.5}$  94°, $^{741.5}$  93.7°, $^{327}$  93.5°, $^{392}$  93°, $^{663}$ ,  
 $^{787a}$ ,  $^{787d}$  93.8°;  $d$  115/4 1.647; $^{73}$  parachor 575.3, $^{74}$  575.9. $^{73}$   
 $(2,4,6-Br_3C_6H_2)_2S_2$ ,  $m$ . 132°. $^{787c}$

- $(2,4\text{-BrMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $100^\circ$ .<sup>872</sup>  
 $(3,4\text{-BrMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $88^\circ$ .<sup>872</sup>  
 $(2,5,4\text{-Br}_2\text{MeC}_6\text{H}_2)_2\text{S}_2$ , m.  $170^\circ$ .<sup>872</sup>  
 $(p\text{-BrC}_6\text{H}_4\text{CH}_2)_2\text{S}_2$ , m.  $88^\circ$ .<sup>403</sup>  
 $(2,3,5\text{-HOBrMeC}_6\text{H}_2)_2\text{S}_2$ , m.  $77^\circ$ ; diBz., m.  $131^\circ$ .<sup>874</sup>  
 $(4\text{-Br-}\alpha\text{-C}_{10}\text{H}_6)_2\text{S}_2$ , m.  $132^\circ$ .<sup>787a, 487d</sup>  
 $(o\text{-IC}_6\text{H}_4)_2\text{S}_2$ , m.  $133^\circ$ .<sup>42</sup>  
 $(p\text{-IC}_6\text{H}_4)_2\text{S}_2$ , m.  $124^\circ$ .<sup>52</sup>  
 $(4,3\text{-IMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $105^\circ$ .<sup>42</sup>  
 $(\alpha\text{-I-}\beta\text{-C}_{10}\text{H}_6)_2\text{S}_2$ , m.  $154^\circ$ .<sup>42</sup>

### Amino-Disulfides

- $(\text{PhCH}_2\text{MeNCH}_2)_2\text{S}_2$ , HCl, m.  $135^\circ$ .<sup>78</sup>  
 $(\text{C}_5\text{H}_{10}\text{NCH}_2)_2\text{S}_2$ , m.  $40^\circ$ ; HCl, m.  $178^\circ$ .<sup>78</sup>  
 $(2\text{-C}_9\text{H}_8\text{N})_2\text{S}_2$ , m.  $137^\circ$ .<sup>681</sup>  
 $(\text{H}_2\text{NCH}_2\text{CH}_2)_2\text{S}_2$ , 2HCl, m.  $216^\circ$ ,<sup>703.7</sup>  $212.5^\circ$ ,<sup>538</sup>  $210^\circ$ ,<sup>111</sup>  $203^\circ$ ; <sup>43,</sup>  
<sup>163</sup> picrate  $198\text{--}200^\circ$ ,<sup>291</sup>  $197^\circ$ ; <sup>577</sup> diBz., m.  $132.5^\circ$ ,<sup>217</sup>  $132^\circ$ .<sup>163, 291</sup>  
 $(\text{MeNHCH}_2\text{CH}_2)_2\text{S}_2$ , 2HCl m.  $205^\circ$ ; picrate, m.  $158^\circ$ .<sup>288</sup>  
 $(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{S}_2$ , MeI decomposes  $230\text{--}5^\circ$ .<sup>658</sup>  
 $(\text{Et}_2\text{NCH}_2\text{CH}_2)_2\text{S}_2$ , b<sub>5</sub>  $125\text{--}35^\circ$ ,<sup>111</sup> b<sub>10</sub>  $160^\circ$ ,<sup>482</sup> b<sub>20</sub>  $155\text{--}60^\circ$ ; <sup>808</sup>  
<sup>2</sup>HCl, m.  $220^\circ$ ; <sup>609</sup> 2HCl·2H<sub>2</sub>O, m.  $219^\circ$ ; <sup>111</sup> 2HBr, m.  $223^\circ$ ,<sup>482</sup>  
 $217^\circ$ .<sup>308</sup>  
 $(\text{PhCH}_2\text{NHCH}_2\text{CH}_2)_2\text{S}_2$ , m.  $269^\circ$ .<sup>184</sup>  
 $(p\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NHCH}_2\text{CH}_2)_2\text{S}_2$ , m.  $146^\circ$ .<sup>472</sup>  
 $(p\text{-H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NHCH}_2\text{CH}_2)_2\text{S}_2$ , m.  $129^\circ$ ; diAc., m.  $196.5^\circ$ .<sup>472</sup>  
 $(\text{H}_2\text{NCH}_2\text{CHMe})_2\text{S}_2$ , 2HCl, m.  $214^\circ$ ; picrate, m.  $163^\circ$ .<sup>291</sup>  
 $(\text{Me}_2\text{NCH}_2\text{CHMe})_2\text{S}_2$ , b<sub>14</sub>  $151\text{--}4^\circ$ ; picrate, m.  $159\text{--}66^\circ$ ; 2MeI,  
m.  $208^\circ$ .<sup>658</sup>  
 $[(\text{CH}_2)_5\text{NCH}_2\text{CHMe}]_2\text{S}_2$ , 2HCl, m.  $226^\circ$ .<sup>769</sup>  
 $[o\text{-C}_6\text{H}_4(\text{CO})_2\text{NCH}_2\text{CHMe}]_2\text{S}_2$ , m.  $161^\circ$ .<sup>725</sup>  
 $(\text{H}_2\text{NCHMeCH}_2)_2\text{S}_2$ , 2HCl, m.  $212^\circ$ ; picrate, m.  $201^\circ$ ; diBz., m.  
 $170^\circ$ .<sup>89</sup>  
 $(\text{Bu}_2\text{NCH}_2\text{CMe}_2)_2\text{S}_2$ , 2HI, m.  $176^\circ$ .<sup>751</sup>  
 $(\text{Me}_2\text{NCH}_2\text{CHPh})_2\text{S}_2$ , m.  $146^\circ$ .<sup>111</sup>  
 $(\text{MeNHCHMeCHPh})_2\text{S}_2$ , 2HCl, m.  $232^\circ$ .<sup>111</sup>  
 $[\text{MeNHCH}_2\text{CH}(\text{C}_6\text{H}_4\text{OH-}m)]_2\text{S}_2$ , m.  $156^\circ$ ; 2HCl, m.  $219^\circ$ ;  
<sup>2</sup>HBr, m.  $186^\circ$ ; diAc., m.  $150^\circ$ .<sup>111</sup>  
 $[\text{MeNHCH}_2\text{CH}(\text{C}_6\text{H}_3(\text{OH})_{2-3,4})]_2\text{S}_2$ , m.  $138^\circ$ ; sulfate, m.  
 $190^\circ$ .<sup>111</sup>  
 $[\text{HCO}(\text{PhCH}_2)\text{NCMe:CH}]_2\text{S}_2$ , m.  $98^\circ$ .<sup>786</sup>

- $(\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2)_2\text{S}_2$ , 2HCl, m.  $219^\circ$ ,<sup>290, 471</sup>  $222^\circ$ ; 2HBr, m.  $232^\circ$ ; picrate, m.  $148^\circ$ ; <sup>472</sup> diBz., m.  $122^\circ$ .<sup>471</sup>  
 $(\text{Et}_2\text{NCH}_2\text{CH}_2\text{CH}_2)_2\text{S}_2$ , b<sub>25</sub>  $175-7^\circ$ ; 2HCl, m.  $221^\circ$ .<sup>308</sup>  
 $[(\text{CH}_2)_5\text{NCH}_2\text{CH}_2\text{CH}_2]_2\text{S}_2$ , 2HCl, m.  $212^\circ$ .<sup>768</sup>  
 $(p\text{-H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NHCH}_2\text{CH}_2\text{CH}_2)_2\text{S}_2$ , diAc., m.  $163^\circ$ .<sup>472</sup>  
 $[\text{H}_2\text{N}(\text{CH}_2)_4\text{CH}_2]_2\text{S}_2$ , b<sub>1</sub>  $135-40^\circ$ ; diBz., m.  $133^\circ$ .<sup>249</sup>  
 $[\text{Me}_2\text{N}(\text{CH}_2)_5\text{CH}_2]_2\text{S}_2$ , b<sub>0.02</sub>  $130^\circ$ ; 2MeI, m.  $196^\circ$ .<sup>554</sup>  
 $(o\text{-H}_2\text{NC}_6\text{H}_4)_2\text{S}_2$ , m.  $93^\circ$ ,<sup>377, 588, 618, 850</sup>  $92.2^\circ$ ,<sup>692</sup>  $92^\circ$ ,<sup>96</sup>  $91^\circ$ ,<sup>294</sup>  $88^\circ$ ; <sup>607, 789</sup> picrate, m.  $141^\circ$ ,<sup>370</sup> diformate, m.  $161^\circ$ ; <sup>808</sup> diAc., m.  $169^\circ$ ,<sup>588</sup>  $167.5^\circ$ ,<sup>618</sup>  $155^\circ$ ,<sup>789</sup>  $154^\circ$ ; <sup>325</sup> diBz., m.  $141^\circ$ .<sup>541</sup>  
 $(o\text{-EtO}_2\text{CCONHC}_6\text{H}_4)_2\text{S}_2$ , m.  $104^\circ$ .<sup>95a</sup>  
 $(o\text{-HO}_2\text{CCH}_2\text{CH}_2\text{CONHC}_6\text{H}_4)_2\text{S}_2$ , m.  $175^\circ$ ,<sup>618</sup>  $168^\circ$ .<sup>95a</sup>  
 $(o\text{-HO}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CONHC}_6\text{H}_4)_2\text{S}_2$ , m.  $156^\circ$ .<sup>95a</sup>  
 $(o\text{-cis-HO}_2\text{CCH:CHCONHC}_6\text{H}_4)_2\text{S}_2$ , m.  $201^\circ$ .<sup>95a</sup>  
 $(o\text{-2-C}_4\text{H}_3\text{O}\cdot\text{CONHC}_6\text{H}_4)_2\text{S}_2$ , m.  $160.5^\circ$ .<sup>95a</sup>  
 $(o\text{-}\alpha\text{-C}_4\text{H}_3\text{S}\cdot\text{CONHC}_6\text{H}_4)_2\text{S}_2$ , m.  $154^\circ$ .<sup>95a</sup>  
 $o\text{-C}_6\text{H}_4(\text{CONHC}_6\text{H}_4)_2\text{S}_2$ , m.  $219^\circ$ .<sup>95a</sup>  
 $(o\text{-H}_2\text{NCO}\cdot\text{CONHC}_6\text{H}_4)_2\text{S}_2$ , m.  $240^\circ$ .<sup>95a</sup>  
 $(o\text{-PhNHCO}\cdot\text{CONHC}_6\text{H}_4)_2\text{S}_2$ , m.  $230^\circ$ .<sup>95a</sup>  
 $(o\text{-PhCH:NC}_6\text{H}_4)_2\text{S}_2$ , m.  $140^\circ$ .<sup>94</sup>  
 $(o\text{-HOC}_6\text{H}_4\text{CH:NC}_6\text{H}_4\text{-}o)_2\text{S}_2$ , m.  $171^\circ$ .<sup>94</sup>  
 $(o\text{-}\alpha\text{-C}_4\text{H}_3\text{O}\cdot\text{CH:NC}_6\text{H}_4)_2\text{S}_2$ , m.  $134.5^\circ$ .<sup>94</sup>  
 $(o\text{-MeNHC}_6\text{H}_4)_2\text{S}_2$ , m.  $68^\circ$ ; <sup>346, 431, 641</sup> 2HI, m.  $110^\circ$ ; picrate, m.  $140^\circ$ ; <sup>431</sup> diformate, m.  $108^\circ$ .<sup>539, 641</sup>  
 $(o\text{-EtNHC}_6\text{H}_4)_2\text{S}_2$ , m.  $72^\circ$ ; <sup>431</sup> diformate, m.  $115^\circ$ .<sup>539</sup>  
 $(o\text{-PhCH}_2\text{NHC}_6\text{H}_4)_2\text{S}_2$ , m.  $104^\circ$ .<sup>431</sup>  
 $(o\text{-HO}_2\text{CCH}_2\text{NHC}_6\text{H}_4)_2\text{S}_2$ , m.  $175^\circ$ .<sup>431</sup>  
 $[2,5\text{-H}_2\text{N}(\text{MeO})\text{C}_6\text{H}_3]_2\text{S}_2$ , m.  $76^\circ$ ; diAc., m.  $203^\circ$ .<sup>371</sup>  
 $[2,4,5\text{-H}_2\text{N}(\text{MeO})_2\text{C}_6\text{H}_2]_2\text{S}_2$ , m.  $175^\circ$ .<sup>270</sup>  
 $[2,5\text{-H}_2\text{N}(\text{EtO})\text{C}_6\text{H}_3]_2\text{S}_2$ , m.  $101^\circ$ .<sup>418</sup>  
 $[2,5\text{-H}_2\text{N}(\text{NC})\text{C}_6\text{H}_3]_2\text{S}_2$ , m.  $188^\circ$ .<sup>98</sup>  
 $(2,3\text{-H}_2\text{NMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $84^\circ$ ; picrate  $134^\circ$ ; 2HCl, m.  $197^\circ$ .<sup>370</sup>  
 $(2,5\text{-H}_2\text{NMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $89^\circ$ ; diAc., m.  $206^\circ$ .<sup>406</sup>  
 $(2,5\text{-MeHNMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $86^\circ$ .<sup>641</sup>  
 $(2,6\text{-H}_2\text{NMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $127^\circ$ .<sup>92b</sup>  
 $[2,4\text{-(H}_2\text{N)}_2\text{C}_6\text{H}_3]_2\text{S}_2$ , m.  $148^\circ$ .<sup>149</sup>  
 $[2,4,5\text{-(H}_2\text{N)}_2(\text{AcNH})\text{C}_6\text{H}_2]_2\text{S}_2$ , 2HCl, m.  $298^\circ$ .<sup>408</sup>  
 $(m\text{-H}_2\text{NC}_6\text{H}_4)_2\text{S}_2$ , m.  $60^\circ$ ,<sup>243</sup>  $52^\circ$ ; <sup>876</sup> diAc., m.  $213^\circ$ ,<sup>242</sup>  $210^\circ$ .<sup>876</sup>  
 $(m\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{S}_2$ , b<sub>16</sub>  $162-6^\circ$ ; 2MeI, m.  $186^\circ$ .<sup>876</sup>  
 $[3,4\text{-(H}_2\text{N)}_2\text{C}_6\text{H}_3]_2\text{S}_2$ , m.  $151^\circ$ .<sup>850</sup>

- (3,4- $\text{H}_2\text{NMeC}_6\text{H}_3$ ) $_2\text{S}_2$ , m.  $82^\circ$ ; diAc., m.  $239^\circ$ .<sup>240</sup>  
 (5,2- $\text{H}_2\text{NMeC}_6\text{H}_3$ ) $_2\text{S}_2$ , m.  $94^\circ$ .<sup>877</sup>  
 (*p*- $\text{H}_2\text{NC}_6\text{H}_4$ ) $_2\text{S}_2$ , m.  $82^\circ$ ,<sup>476</sup>  $80^\circ$ ,<sup>378</sup>  $73^\circ$ ,<sup>79^\circ</sup>,<sup>698</sup>  $77^\circ$ ,<sup>176</sup>  $367^\circ$ ,<sup>d</sup>  $76^\circ$ ,<sup>623b</sup>,  
<sup>850</sup>  $75^\circ$ ; <sup>70</sup>  $2\text{HCl}$ , m.  $225^\circ$ ; <sup>50</sup>, <sup>369</sup> diAc., m.  $218^\circ$ ,<sup>239</sup>  $314^\circ$ ,<sup>176</sup>,  
<sup>698</sup>  $216^\circ$ ,<sup>248</sup>  $215^\circ$ ,<sup>70</sup>  $314$ ,  $367^\circ$ ,<sup>c</sup>  $367^\circ$ ,<sup>d</sup>  $427$ ,  $873^\circ$ ,<sup>176</sup>  $214^\circ$ ,<sup>476</sup>  $205^\circ$ ; <sup>734</sup>  $\alpha$ - m.  
 $184^\circ$ ,<sup>314</sup>  $182^\circ$ ,<sup>314</sup>,  $367^\circ$ ,<sup>c</sup>  $367^\circ$ ,<sup>d</sup>  $378$ ,  $427^\circ$ ,<sup>180^\circ</sup>,<sup>873</sup>  $+1\text{H}_2\text{O}$ , m.  $122^\circ$ ,  
 $+1/2\text{H}_2\text{O}$ , m.  $130^\circ$ ; diBz., m.  $264^\circ$ .<sup>367c</sup>  
 (*p*- $\text{H}_2\text{NCONHC}_6\text{H}_4$ ) $_2\text{S}_2$ , m.  $205^\circ$ .<sup>850</sup>  
 (*p*- $\text{PhNHCONHC}_6\text{H}_4$ ) $_2\text{S}_2$ , m.  $286-9^\circ$ .<sup>850</sup>  
 (*p*- $\text{PhNHCSNHC}_6\text{H}_4$ ) $_2\text{S}_2$ , m.  $157.5^\circ$ .<sup>850</sup>  
 (*p*- $\text{H}_2\text{C}:\text{NC}_6\text{H}_4$ ) $_2\text{S}_2$ , m.  $60-79^\circ$ .<sup>850</sup>  
 (*p*- $\text{HO}_2\text{CCH}_2\text{NHC}_6\text{H}_4$ ) $_2\text{S}_2$ , m.  $189^\circ$ .<sup>850</sup>  
 [*p*-(*p*- $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NH}$ ) $\text{C}_6\text{H}_4$ ] $_2\text{S}_2$ , m.  $220^\circ$ ; diAc., m.  $171^\circ$ .<sup>850</sup>  
 (*p*- $\text{MeNHC}_6\text{H}_4$ ) $_2\text{S}_2$ ,  $2\text{HCl}$ , m.  $163^\circ$ .<sup>850</sup>  
 (*p*- $\text{Me}_2\text{NC}_6\text{H}_4$ ) $_2\text{S}_2$ , m.  $118^\circ$ .<sup>17</sup>, <sup>243</sup>, <sup>469</sup>, <sup>476</sup>, <sup>531</sup>, <sup>850</sup>  
 (*p*- $\text{Et}_2\text{NC}_6\text{H}_4$ ) $_2\text{S}_2$ , m.  $72^\circ$ .<sup>383</sup>  
 (4,3- $\text{H}_2\text{NCIC}_6\text{H}_3$ ) $_2\text{S}_2$ , m.  $147^\circ$ .<sup>672</sup>  
 (4,2- $\text{H}_2\text{NMeC}_6\text{H}_3$ ) $_2\text{S}_2$ , m.  $113.5^\circ$ ;  $2\text{HCl}$ , m.  $213^\circ$ .<sup>850</sup>  
 (4,3- $\text{H}_2\text{NMeC}_6\text{H}_3$ ) $_2\text{S}_2$ , m.  $112^\circ$ ; <sup>368a</sup>, <sup>370</sup>, <sup>850</sup> diAc., m.  $225^\circ$ ; <sup>368a</sup>  
 picrate, m.  $179^\circ$ .<sup>370</sup>  
 [4,3- $\text{H}_2\text{N}(\text{MeO})\text{C}_6\text{H}_3$ ] $_2\text{S}_2$ , m.  $88^\circ$ ; <sup>371</sup>, <sup>850</sup> diAc., m.  $136^\circ$ .<sup>371</sup>  
 [4,3- $\text{H}_2\text{N}(\text{H}_2\text{NSO}_2)\text{C}_6\text{H}_3$ ] $_2\text{S}_2$ , m.  $247^\circ$ .<sup>850</sup>  
 ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{C}_6\text{H}_4$ ) $_2\text{S}_2$ ,  $\text{HCl}$ , m.  $340.5^\circ$ ; Bz., m.  $201^\circ$ .<sup>428</sup>  
 (*o*- $\text{H}_2\text{NC}_6\text{H}_4\text{CH}_2$ ) $_2\text{S}_2$ , m.  $91^\circ$ ,<sup>292</sup> propionate, m.  $191^\circ$ .<sup>430</sup>  
 (*p*- $\text{H}_2\text{NC}_6\text{H}_4\text{CH}_2$ ) $_2\text{S}_2$ , m.  $98^\circ$ ; Ac., m.  $174^\circ$ .<sup>799</sup>  
 (*p*- $\text{Me}_2\text{NC}_6\text{H}_4\text{CH}_2$ ) $_2\text{S}_2$ , m.  $83.5^\circ$ ;  $\text{HCl}$ , m.  $211^\circ$ .<sup>512</sup>  
 [(*p*- $\text{Me}_2\text{NC}_6\text{H}_4$ ) $_2\text{CH}$ ] $_2\text{S}_2$ , m.  $164^\circ$ .<sup>67.5</sup>  
 (4- $\text{H}_2\text{N}-\alpha\text{-C}_{10}\text{H}_8$ ) $_2\text{S}_2$ , m.  $168^\circ$ ; diAc., m.  $265^\circ$ .<sup>879</sup>  
 (8- $\text{H}_2\text{N}-\alpha\text{-C}_{10}\text{H}_8$ ) $_2\text{S}_2$ , m.  $118^\circ$ .<sup>654</sup>  
 (4- $\text{H}_2\text{N}-\alpha\text{-C}_{14}\text{H}_6\text{O}_2$ ) $_2\text{S}_2$ , (anthraquinone), m.  $> 300^\circ$ .<sup>296b</sup>  
 (4- $\text{MeNH}-\alpha\text{-C}_{14}\text{H}_6\text{O}_2$ ) $_2\text{S}_2$ , m.  $280^\circ$ .<sup>296b</sup>  
 (5- $\text{MeNH}-\alpha\text{-C}_{14}\text{H}_6\text{O}_2$ ) $_2\text{S}_2$ , m.  $321^\circ$ .<sup>296b</sup>  
 (4- $\text{Me}_2\text{N}-\alpha\text{-C}_{14}\text{H}_6\text{O}_2$ ) $_2\text{S}_2$ , m.  $220^\circ$  with decomposition.<sup>296b</sup>  
 (5- $\text{Me}_2\text{N}-\alpha\text{-C}_{14}\text{H}_6\text{O}_2$ ) $_2\text{S}_2$ , m.  $272^\circ$ .<sup>296b</sup>

### Nitro-Disulfides

- (*o*- $\text{O}_2\text{NC}_6\text{H}_4\text{S}^\cdot$ ) $_2$ , m.  $199^\circ$ ,<sup>871</sup>  $198^\circ$ ,<sup>176</sup>, <sup>268</sup>, <sup>347</sup>, <sup>469</sup>  $196^\circ$ ,<sup>494</sup>, <sup>880</sup>  
 $195^\circ$ ,<sup>85c</sup>, <sup>85d</sup>, <sup>218</sup>, <sup>486</sup>, <sup>541</sup>, <sup>789</sup>  $193^\circ$ ,<sup>561</sup>  $150^\circ$ ,<sup>375</sup> parachor 665.3 at  
 $125^\circ$ .<sup>74</sup>

- $(m\text{-O}_2\text{NC}_6\text{H}_4\text{S}\cdot)_2$ , m.  $84^\circ$ ,<sup>106, 476</sup>  $83^\circ$ ,<sup>157</sup>  $82^\circ$ .<sup>252, 480</sup>  
 $(p\text{-O}_2\text{NC}_6\text{H}_4\text{S}\cdot)_2$ , m.  $184^\circ$ ,<sup>327</sup>  $182^\circ$ ,<sup>279</sup>  $181^\circ$ ,<sup>66, 107, 140, 268, 547, 846,</sup>  
<sup>875</sup>  $180.5^\circ$ ,<sup>39</sup>  $180^\circ$ ,<sup>284, 375</sup>  $170^\circ$ ,<sup>476</sup> 2 forms, m.  $181^\circ$  and  $170^\circ$ ,  
 transition  $134^\circ$ ,<sup>218</sup> dipole moment  $4.31 \times 10^{-18}$ .<sup>327</sup>  
 $(p\text{-O}_2\text{NC}_6\text{H}_4)_2\text{S}^{35}_2$ , 3 forms, m.  $134^\circ$ ,  $165^\circ$ , and  $179^\circ$ .<sup>7</sup>  
 $[2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3]_2\text{S}_2$ , m.  $280^\circ$ .<sup>218</sup>  
 $[3,5\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3]_2\text{S}_2$ , m.  $177.5^\circ$ .<sup>443</sup>  
 $(2,4\text{-O}_2\text{NClC}_6\text{H}_3)_2\text{S}_2$ , m.  $212.8^\circ$ ,<sup>218</sup>  $212^\circ$ ,<sup>85d, 375, 868</sup>  $213^\circ$ .<sup>61</sup>  
 $(4,3\text{-O}_2\text{NClC}_6\text{H}_3)_2\text{S}_2$ , m.  $129^\circ$ .<sup>672</sup>  
 $(5,2\text{-O}_2\text{NClC}_6\text{H}_3\text{CH}_2)_2\text{S}_2$ , m.  $155.5^\circ$ .<sup>755b</sup>  
 $(2,4,6\text{-O}_2\text{NCl}_2\text{C}_6\text{H}_2)_2\text{S}_2$ , m.  $190^\circ$ .<sup>85e</sup>  
 $(2,4\text{-O}_2\text{NBrC}_6\text{H}_3)_2\text{S}_2$ , m.  $174^\circ$ .<sup>218</sup>  
 $[2,4\text{-O}_2\text{N(H}_2\text{N)C}_6\text{H}_3]_2\text{S}_2$ , m.  $222^\circ$ .<sup>561</sup>  
 $[3,4\text{-O}_2\text{N(H}_2\text{N)C}_6\text{H}_3]_2\text{S}_2$ , m.  $169^\circ$ .<sup>144, 850</sup>  
 $[4,2\text{-O}_2\text{N(H}_2\text{N)C}_6\text{H}_3]_2\text{S}_2$ , m.  $178^\circ$ ; diAc., m.  $263^\circ$ ; diBz., m.  
 $215^\circ$ .<sup>267</sup>  
 $[4,3\text{-O}_2\text{N(H}_2\text{N)C}_6\text{H}_3]_2\text{S}_2$ , Ac., m.  $193^\circ$ .<sup>371</sup>  
 $[5,2\text{-O}_2\text{N(H}_2\text{N)C}_6\text{H}_3]_2\text{S}_2$ , m.  $237^\circ$ ,<sup>405</sup>  $222^\circ$ .<sup>96</sup>  
 $[2,5,4\text{-O}_2\text{N(HO)ClC}_6\text{H}_2]_2\text{S}_2$ , m.  $277^\circ$ ; diAc., m.  $194^\circ$ .<sup>266</sup>  
 $[2,4,5\text{-O}_2\text{N(MeO)}_2\text{C}_6\text{H}_2]_2\text{S}_2$ , m.  $227^\circ$ .<sup>270</sup>  
 $[4,2\text{-O}_2\text{N(PhCH}_2\text{O)C}_6\text{H}_3]_2\text{S}_2$ , m.  $161^\circ$ .<sup>10</sup>  
 $[4,5\text{-O}_2\text{N(MeS)C}_6\text{H}_3]_2\text{S}_2$ , m.  $217^\circ$ .<sup>371</sup>  
 $[5,2\text{-O}_2\text{N(p-MeC}_6\text{H}_4\text{S)C}_6\text{H}_3]_2\text{S}_2$ , m.  $154^\circ$ .<sup>267</sup>  
 $(2,4\text{-O}_2\text{NMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $175^\circ$ .<sup>363</sup>  
 $(2,6\text{-O}_2\text{NMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $149^\circ$ .<sup>92b</sup>  
 $(5,2\text{-O}_2\text{NMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $148^\circ$ .<sup>443</sup>  
 $(3,4\text{-O}_2\text{NMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $82^\circ$ .<sup>240</sup>  
 $(4,2\text{-O}_2\text{NMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $188^\circ$ .<sup>612</sup>  
 $(4,3\text{-O}_2\text{NMeC}_6\text{H}_3)_2\text{S}_2$ , m.  $163^\circ$ .<sup>370</sup>  
 $(o\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2)_2\text{S}_2$ , m.  $112.0^\circ$ ,<sup>73</sup>  $109.5^\circ$ ,<sup>626</sup>  $47^\circ$ ; <sup>409</sup> d 115/4  
 1.308; parachor 665.7.<sup>73</sup>  
 $(m\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2)_2\text{S}_2$ , m.  $104^\circ$ ,<sup>496</sup>  $103^\circ$ .<sup>626</sup>  
 $(p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2)_2\text{S}_2$ , m.  $126.5^\circ$ ,<sup>386, 626</sup>  $126^\circ$ .<sup>786</sup>  
 $(2\text{-O}_2\text{N-}\alpha\text{-C}_{10}\text{H}_6)_2\text{S}_2$ , m.  $176^\circ$ .<sup>372</sup>  
 $(4\text{-O}_2\text{N-}\alpha\text{-C}_{10}\text{H}_6)_2\text{S}_2$ , m.  $189^\circ$ .<sup>372</sup>  
 $(5\text{-O}_2\text{N-}\alpha\text{-C}_{10}\text{H}_6)_2\text{S}_2$ , m.  $233^\circ$ .<sup>374</sup>  
 $(8\text{-O}_2\text{N-}\alpha\text{-C}_{10}\text{H}_6)_2\text{S}_2$ , m.  $214^\circ$ .<sup>654</sup>  
 $(1\text{-O}_2\text{N-}\beta\text{-C}_{10}\text{H}_6)_2\text{S}_2$ , m.  $190^\circ$ .<sup>372</sup>  
 $(7\text{-O}_2\text{N-}\beta\text{-C}_{10}\text{H}_6)_2\text{S}_2$ , m.  $265^\circ$ .<sup>374</sup>



Some bis-Nitro-Disulfides <sup>320</sup>

n	m.p. °C	n	m.p. °C
2	203°	7	127°
3	160°	8	153°
4	195°	9	115°
5	148°	10	147°
6	160°	12	142°

$\text{S}(\text{CH}_2\text{CH}_2\text{SSC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_2$ , m. 148°. <sup>320</sup>

## Unsymmetrical Disulfides

$\text{MeSSCCl}_3$ ,  $b_{13}$  77–8°;  $d_{25}$  1.526;  $n$  15/D 1.575. <sup>30</sup>

$\text{MeSSEt}$ , m. –89.83°; <sup>79</sup> b. 129.7°, <sup>520</sup> 135°, <sup>113.7</sup>  $b_{57}$  58°; <sup>79</sup>  $d_{20}$  1.0224, <sup>79</sup>  $d$  20/4 1.025;  $n$  20/D 1.5145, <sup>520</sup> 1.5146. <sup>79</sup>

$\text{MeSSBu}$ ,  $b_{22}$  77.5–8.5°. <sup>436a</sup>, <sup>436b</sup>

$\text{MeSSCMe}_3$ , m. –51.197°;  $b_{42}$  69°;  $d_{20}$  0.9629;  $n$  20/D 1.4975. <sup>79</sup>

$\text{MeSSC}_8\text{H}_{17}$ ,  $b_{0.3}$  65–8°. <sup>436b</sup>

$\text{MeSSCH}_2\text{CH}_2\text{OH}$ ,  $b_{20}$  112.5–3.5°. <sup>436b</sup>

$\text{MeSSC}_{10}\text{H}_{17}$ , fenchyl,  $b_{20}$  146–8°. <sup>457</sup>

$\text{ClCH}_2\text{SSEt}$ ,  $b_8$  56°,  $b_{15}$  73–4°, <sup>200</sup>  $b_{16}$  93–100°; <sup>114.5</sup>  $d$  0/4 1.258,  $d$  20/4 1.230;  $n$  20/D 1.5428. <sup>200</sup>

$\text{ClCH}_2\text{SSPh}$ ,  $b_6$  127–9°;  $d$  0/4 1.342,  $d$  20/4 1.323;  $n$  20/D 1.6290. <sup>200</sup>

$\text{Cl}_2\text{CHSSEt}$ ,  $b_{13}$  87°;  $d$  0/4 1.377,  $d$  20/4 1.353;  $n$  20/D 1.5513. <sup>200</sup>

$\text{Cl}_3\text{CSSEt}$ ,  $b_{14}$  91–2°, <sup>30</sup>  $b_5$  82°,  $b_{20}$  100°;  $d$  0/4 1.475,  $d$  20/4 1.452, <sup>200</sup>  $d_{25}$  1.439;  $n$  15/D 1.561, <sup>30</sup>  $n$  20/D 1.5571. <sup>200</sup>

$\text{Cl}_3\text{CSSPr}$ ,  $b_{12}$  104–4.5°;  $d_{25}$  1.374;  $n$  15/D 1.548. <sup>30</sup>

$\text{Cl}_3\text{CSSCHMe}_2$ ,  $b_{30}$  116.5–7°;  $d_{25}$  1.360;  $n$  18/D 1.546. <sup>30</sup>

$\text{Cl}_3\text{CSSBu}$ ,  $b_{10.5}$  118–9°;  $d_{25}$  1.321;  $n$  25/D 1.538. <sup>30</sup>

$\text{Cl}_3\text{CSSCMe}_3$ ,  $b_{12}$  107–8°;  $d_{25}$  1.317;  $n$  25/D 1.540. <sup>30</sup>

$\text{Cl}_3\text{CSSCH}_2\text{CH:CH}_2$ ,  $b_{10.5}$  100–1°;  $d_{25}$  1.414;  $n$  15/D 1.570. <sup>30</sup>

$\text{Cl}_3\text{CSSCEt}_2\text{Me}$ ,  $b_4$  118–20°;  $d_{25}$  1.278;  $n$  25/D 1.541. <sup>30</sup>

$\text{Cl}_3\text{SSC}_6\text{H}_{11}$ ,  $b_{14}$  156–8°;  $d_{25}$  1.400;  $n$  25/D 1.563. <sup>30</sup>

$\text{Cl}_3\text{CSSPh}$ ,  $b_4$  123–6°;  $d_{25}$  1.447;  $n$  25/D 1.623. <sup>30</sup>

$\text{Cl}_3\text{CSSCH}_2\text{Ph}$ ,  $b_5$  153–8°;  $d_{25}$  1.411;  $n$  25/D 1.613. <sup>30</sup>

$\text{Cl}_3\text{SSC}_6\text{H}_4\text{Me-}o$ ,  $b_4$  150.5–1.5°;  $d_{20}$  1.403;  $n$  15/D 1.618. <sup>30</sup>

$\text{Cl}_3\text{SSC}_6\text{H}_4\text{Me-}m$ ,  $b_{2.5}$  139.5–40°;  $d_{25}$  1.405;  $n$  15/D 1.618. <sup>30</sup>

- $\text{Cl}_3\text{CSSC}_6\text{H}_4\text{Me-}p$ ,  $b_3$  141–4°;  $d_{25}$  1.400;  $n$  25/D 1.617.<sup>30</sup>  
 $\text{Cl}_3\text{CSSC}_6\text{H}_4\text{CMe}_3\text{-}p$ ,  $b_2$  151–3°;  $d_{25}$  1.286;  $n$  15/D 1.591.<sup>30</sup>  
 $\text{Cl}_3\text{CSSC}_6\text{H}_4\text{Cl-}o$ ,  $b_8$  170.5–2°;  $n$  20/D 1.635.<sup>30</sup>  
 $\text{Cl}_3\text{CSSC}_6\text{H}_4\text{Cl-}p$ ,  $m$ . 56.5°;  $b_2$  154–5°.<sup>30</sup>  
 $\text{Cl}_3\text{CSSC}_6\text{H}_4\text{NO}_2\text{-}o$ ,  $m$ . 70.5°.<sup>30</sup>  
 $\text{Cl}_3\text{CSSC}_6\text{H}_4\text{NO}_2\text{-}m$ ,  $b_2$  132–3°;  $d_{20}$  1.292;  $n$  15/D 1.607.<sup>30</sup>  
 $\text{Cl}_3\text{CSSC}_6\text{H}_4\text{NO}_2\text{-}p$ ,  $m$ . 67°.<sup>30</sup>  
 $\text{EtSSCH}_2\text{CHCl}_2$ ,  $b_2$  103–5°.<sup>439</sup>  
 $\text{EtSSPr}$ ,  $b$ . 172.6°,<sup>520</sup> 173°;<sup>500</sup>  $d$  20/4 0.9739,<sup>520</sup> 0.9746,  $d$  25/4 0.9700;  $n$  20/D 1.5019,<sup>500</sup> 1.5014,<sup>520</sup>  $n$  25/D 1.4995.<sup>500</sup>  
 $\text{EtSSCHMe}_2$ ,  $b$ . 165°;  $d$  20/4 0.9661,  $d$  25/4 0.9613;  $n$  20/D 1.4988,  $n$  25/D 1.4963.<sup>500</sup>  
 $\text{EtSSBu}$ ,  $b$ . 193°;  $d$  20/4 0.9594,  $d$  25/4 0.9548;  $n$  20/D 1.4984,  $n$  25/D 1.4961.<sup>500</sup>  
 $\text{EtSSCH}_2\text{CHMe}_2$ ,  $b$ . 184°;  $d$  20/4 0.9543,  $d$  25/4 0.9497;  $n$  20/D 1.4951,  $n$  25/D 1.4926.<sup>500</sup>  
 $\text{EtSSCHMeEt}$ ,  $b$ . 181°;  $d$  20/4 0.9603,  $d$  25/4 0.9556;  $n$  20/D 1.4986,  $n$  25/D 1.4964.<sup>500</sup>  
 $\text{EtSSCMe}_3$ ,  $m$ . –66.71°;  $b$ . 175°,<sup>500</sup>  $b_{90}$  66°,  $b_{93}$  68°,  $b_{97}$  80°; <sup>666</sup>  $d$  20/4 0.9471,  $d$  25/4 0.9425;  $n$  20/D 1.4942,  $n$  25/D 1.4916.<sup>500</sup>  
 $\text{EtSSPh}$ ,  $b_{15}$  126°.<sup>113.7</sup>  
 $\text{EtSSC}_{10}\text{H}_7\text{-}\beta$ ,  $b_2$  162°.<sup>469</sup>  
 $\text{EtSSCH}_2\text{SEt}$ ,  $b_{16}$  125–7°.<sup>114.5</sup>  
 $\text{EtSSCH}_2\text{SPh}$ ,  $m$ . 52°;  $b_{14}$  198–200°.<sup>114.5</sup>  
 $\text{PrSSCHMe}_2$ ,  $b$ . 184°;  $d$  20/4 0.9506,  $d$  25/4 0.9462;  $n$  20/D 1.4943,  $n$  25/D 1.4920.<sup>500</sup>  
 $\text{PrSSCH}_2\text{CH:CH}_2$ ,  $b_{16}$  66–69°;  $d_{15}$  1.0231.<sup>728</sup>  
 $\text{BuSSPh}$ ,  $b_3$  82–3°,<sup>401</sup>  $b_{12}$  140–5°.<sup>113.7</sup>  
 $s\text{-BuSSCH}_2\text{CH:CH}_2$ ,  $b_{10}$  82–4°.<sup>514</sup>  
 $t\text{-BuSSCMe}_2\text{Et}$ , 2 phases,  $m$ . –58.231° and –58.197°;  $b_{13}$  97°;  $d_{20}$  0.9291;  $n$  20/D 1.4943.<sup>79</sup>  
 $t\text{-BuSSC}_{10}\text{H}_7\text{-}\beta$ ,  $m$ . 53°.<sup>660, 666</sup>  
 $\text{HO(CH}_2)_6\text{SS(CH}_2)_6\text{Cl}$ ,  $b_{0.1}$  193–5°;  $n$  22/D 1.525.<sup>824</sup>  
 $\text{HO(CH}_2)_6\text{SS(CH}_2)_6\text{CN}$ ,  $b_{0.7}$  212–7°;  $n$  19.5°D 1.529.<sup>824</sup>  
 $\text{PhSSCH}_2\text{COMe}$ ,  $b_{0.4}$  102–3°.<sup>400</sup>  
 $\text{PhSSCH}_2\text{COBu}$ ,  $b_{0.2}$  125–30°.<sup>400</sup>  
 $\text{PhSSC}_6\text{H}_4\text{COMe}$ ,  $m$ . 60°.<sup>464</sup>  
 $\text{PhSSC}_6\text{H}_4\text{NO}_2\text{-}o$ ,  $m$ . 55°,<sup>469, 494</sup> 50°.<sup>176, 464</sup>  
 $\text{PhSSC}_6\text{H}_4\text{NO}_2\text{-}m$ , oil.<sup>464</sup>

- $\text{PhSSC}_6\text{H}_4\text{NO}_2$ -*p*, m.  $58.5^\circ$ ,<sup>176</sup>  $58^\circ$ .<sup>464</sup>  
 $\text{PhSSC}_6\text{H}_3(\text{NO}_2)$ -2,4, m.  $87^\circ$ .<sup>176</sup>  
 $\text{PhSSC}_6\text{H}_4\text{OH}$ -*p*, Bz., m.  $104.5^\circ$ .<sup>508</sup>  
 $\text{PhSSC}_6\text{H}_4\text{SO}_2\text{Me}$ , m.  $55^\circ$ .<sup>464</sup>  
 $\text{PhSSC}_{10}\text{H}_7$ - $\beta$ , m.  $76^\circ$ ,<sup>469</sup>  $67.5^\circ$ .<sup>221.5</sup>  
 $\text{PhCH}_2\text{SSC}_6\text{H}_4\text{NO}_2$ -*o*, m.  $54^\circ$ ,<sup>250</sup>  $55^\circ$ .<sup>469</sup>  
 $\text{PhCH}_2\text{SSC}_{14}\text{H}_9$ -9, (anthracene), m.  $128^\circ$ .<sup>250</sup>  
 $o$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NO}_2$ -*o*, m.  $103.5^\circ$ .<sup>176</sup>  
 $o$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NO}_2$ -*p*, m.  $84.5^\circ$ .<sup>176</sup>  
 $o$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_3(\text{NO}_2)$ -2,4, m.  $100.5^\circ$ .<sup>176</sup>  
 $o$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{OH}$ -*p*, Bz., m.  $69.5^\circ$ .<sup>508</sup>  
 $o$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_3(\text{NHAc})\text{Cl}$ -4,3, m.  $100^\circ$ .<sup>176</sup>  
 $m$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NO}_2$ -*o*, m.  $75.5^\circ$ .<sup>176</sup>  
 $m$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_3(\text{NO}_2)$ -2,4, m.  $75.5^\circ$ .<sup>176</sup>  
 $m$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{OH}$ -*p*, Bz., m.  $76^\circ$ .<sup>508</sup>  
 $m$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_3(\text{NHAc})\text{Cl}$ -4,3, m.  $94.5^\circ$ .<sup>176</sup>  
 $p$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NO}_2$ -*o*, m.  $74^\circ$ .<sup>176</sup>  
 $p$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NO}_2$ -*p*, m.  $62.5^\circ$ .<sup>176</sup>  
 $p$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_3(\text{NO}_2)$ -2,4, m.  $115^\circ$ .<sup>176</sup>  
 $p$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{OH}$ -*p*, Bz., m.  $116.5^\circ$ .<sup>508</sup>  
 $p$ - $\text{MeC}_6\text{H}_4\text{SSC}_6\text{H}_3(\text{NHAc})\text{Cl}$ -4,3, m.  $114^\circ$ .<sup>176</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSCHPhCHPhCl}$ , m.  $118.5^\circ$ .<sup>347</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSCH:CPh}_2$ , m.  $121.5^\circ$ .<sup>347</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSCH}_2\text{COMe}$ , m.  $112^\circ$ .<sup>347</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSCH}_2\text{COPh}$ , m.  $84.5^\circ$ .<sup>347</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_{10}\text{Cl}$ -2, m.  $83.5^\circ$ .<sup>347</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_3\text{Cl}_2$ -2,5, m.  $116^\circ$ .<sup>116</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_3\text{Br}_2$ -2,5, m.  $138^\circ$ .<sup>116</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NO}_2$ -*p*, m.  $159.6^\circ$ .<sup>494</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_3(\text{NO}_2)$ -2,4, m.  $176^\circ$ .<sup>494</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{OH}$ -*p*, m.  $151.5^\circ$ ,<sup>347</sup>  $138^\circ$ ; Ac., m.  $67^\circ$ ; Bz., m.  $114^\circ$ .<sup>508</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NMe}_2$ -*p*, m.  $117^\circ$ .<sup>468, 469</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SS-}\alpha$ - $\text{C}_{10}\text{H}_6\text{OH}$ -2, m.  $147^\circ$ .<sup>347</sup>  
 $o$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_{14}\text{H}_9$ - $\alpha$ , (anthracene), m.  $151^\circ$ .<sup>347</sup>  
 $m$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_3\text{Cl}_2$ -2,5, m.  $91^\circ$ .<sup>742</sup>  
 $m$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_3(\text{NO}_2)$ -2,4, m.  $145^\circ$ .<sup>464</sup>  
 $p$ - $\text{O}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_3(\text{NO}_2)$ -2,4, m.  $162^\circ$ .<sup>464</sup>  
 $p$ - $\text{NO}_2\text{C}_6\text{H}_4\text{SSC}_6\text{H}_4\text{OH}$ -*p*, m.  $119^\circ$ .<sup>508</sup>  
 $2,4$ -( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_3\text{SSC}_6\text{H}_3\text{Cl}_2$ -2,4, m.  $140^\circ$ .<sup>754</sup>

$p$ - $\text{HOC}_6\text{H}_4\text{SSC}_{14}\text{H}_7\text{O}_2$ - $\beta$ , (anthraquinone), m.  $193^\circ$ , Bz., m.  $156.5^\circ$ .<sup>508</sup>

$\alpha$ - $\text{C}_{10}\text{H}_7\text{SSC}_{10}\text{H}_7$ - $\beta$ ,  $b_{15}$   $290-1^\circ$ .<sup>14</sup>

### Some Miscellaneous Disulfides

$\text{S}_2(\text{CH}_2\text{CH}_2\text{SH})_2$ , b.  $258^\circ$ ,  $b_{40}$   $180^\circ$ .<sup>649</sup>

$\text{S}_2(\text{CH}_2\text{CH}_2\text{SCH}_2\text{Ph})_2$ , m.  $70^\circ$ .<sup>276</sup>

$\text{S}_2[\text{CH}_2(\text{CH}_2)_5\text{SCN}]_2$ ,  $b_{0.15}$   $201-17^\circ$ ; n 20/D 1.5361.<sup>824</sup>

$\text{S}_2(\text{C}_6\text{H}_4\text{CN}-p)_2$ , m.  $173^\circ$ .<sup>50, 503</sup>

$\text{S}_2(\text{C}_6\text{H}_4\text{SO}_2\text{Me}-p)_2$ , m.  $188^\circ$ ,<sup>126</sup>  $190-2^\circ$ .<sup>97.5</sup>

Cholesteryl disulfide, m.  $144.5^\circ$ ;  $[\alpha]_D$   $-41.78^\circ$ .<sup>828</sup>

### Disulfide Acids

$\text{S}_2(\text{CH}_2\text{COOH})_2$ , m.  $109^\circ$ ,<sup>380c</sup>  $108^\circ$ ,<sup>75a, 627a</sup>  $103^\circ$ ,<sup>775b</sup>  $100^\circ$ ; <sup>85b, 435b</sup> K 0.065; <sup>380b, 594</sup> amide, m.  $158.5^\circ$ ,<sup>5</sup>  $155^\circ$ ,<sup>435b</sup>  $149^\circ$ ; <sup>380a</sup> anilide, m.  $164^\circ$ ,<sup>326</sup>  $161^\circ$ ,<sup>55</sup>  $160^\circ$ ; <sup>716</sup> N-methylanilide, m.  $81^\circ$ ,<sup>668</sup> toluides, *ortho*, m.  $165^\circ$ ; *meta*, m.  $163^\circ$ ; *para*, m.  $182^\circ$ ; <sup>55</sup> naphthalide,  $\alpha$ - m.  $206^\circ$ ;  $\beta$ - m.  $198^\circ$ ; <sup>668</sup> Me ester  $b_{14}$   $154^\circ$ ; <sup>627a</sup> d 16/4 1.2905, d 25/4 1.2809; n 16/D 1.51517, n 25/D 1.51137; <sup>627d</sup> Et ester b.  $280^\circ$ ,<sup>435</sup>  $b_{14}$   $164^\circ$ ; <sup>627a</sup> d 16/4 1.2036, d 25/4 1.1945; n 16/D 1.50085, n 25/D 1.4979; <sup>627d</sup> Pr ester  $b_{0.1}$   $104-6^\circ$ ,<sup>564</sup>  $b_8$   $177-80^\circ$ ; <sup>224</sup> d 25/4 1.1348; n 25/D 1.4903; <sup>564</sup> *i*-Pr ester  $b_{0.1}$   $91-3^\circ$ ; d 25/4 1.1208; n 25/D 1.4838; <sup>564</sup> Bu ester  $b_{0.1}$   $121.5^\circ$ ; d 25/4 1.0986; n 25/D 1.4870; <sup>564</sup> *i*-Bu ester  $b_{0.1}$   $112-4^\circ$ ,<sup>564</sup>  $b_2$   $173^\circ$ ; <sup>224</sup> d 25/4 1.0905; n 25/D 1.4839; <sup>564</sup> Oct ester  $b_{0.5}$   $202-7^\circ$ ; <sup>224, 564</sup> d 25/4 1.0067; n 25/D 1.4780; <sup>564</sup> Dodec ester d 25/4 0.9660; n 25/D 1.4769; <sup>564</sup> Tetradec ester, m.  $35^\circ$ ; <sup>224, 564</sup> Hexadec ester, m.  $44.5^\circ$ ; <sup>224, 564</sup> Octadec ester, m.  $52.5^\circ$ ; <sup>564</sup> Cyclohexyl ester, m.  $56^\circ$ ; <sup>224, 564</sup>  $\text{MeOCH}_2\text{CH}_2$ -ester  $b_{0.3}$   $150-4^\circ$ ; d 25/4 1.2302; n 25/D 1.4990; <sup>564</sup> Choline iodide ester, m.  $157^\circ$ .<sup>326</sup>

$\text{S}_2(\text{CHMeCOOH})_2$ , m.  $142^\circ$ ,<sup>491b, 627a</sup>  $140^\circ$ ,<sup>75a</sup>  $135^\circ$ ; <sup>542, 775b</sup> DL, m.  $150^\circ$ ,<sup>701b</sup>  $149^\circ$ ,  $148.5^\circ$ , meso, m.  $119^\circ$ ; *active*, m.  $117.5^\circ$ ; <sup>261c</sup> D form, m.  $116.5^\circ$ ,  $[\alpha]$  15/D  $60.5^\circ$ ; <sup>491d</sup> K 0.090; <sup>491a</sup> anilide, m.  $160^\circ$ ; <sup>55</sup> Et ester  $b_{14}$   $159^\circ$ ; <sup>627a</sup> d 16/4 1.1398, d 25/4 1.1308; n 16/D 1.49222, n 25/D 1.48822.<sup>627d</sup>

$\text{S}_2(\text{CHEtCOOH})_2$ , anilide, m.  $110^\circ$ ; toluides, *o*- m.  $139^\circ$ , *m*- m.  $146^\circ$ , *p*- m.  $149^\circ$ ; <sup>55</sup> Et ester  $b_{22}$   $187^\circ$ ; <sup>627a</sup> d 16/4 1.0992, d 25/4 1.0909; n 16/D 1.48753, n 25/D 1.48412.<sup>627a</sup>

- $S_2(CMe_2COOEt)_2$ ,  $b_{19}$   $196^\circ$ ;  $^{627a}$  d 16/4 1.1065,  $^{627d}$  d 25/4 1.0980; n 16/D 1.48926, n 25/D 1.48567.  $^{627d}$   
 $S_2(CHPrCOOH)_2$ , m.  $56^\circ$ .  $^{697}$   
 $S_2[CH(CHMe_2)COOEt]_2$ ,  $b_{12}$   $173^\circ$ ;  $^{627a}$  d 16/4 1.0680; d 25/4 1.0602; n 16/D 1.48423, n 25/D 1.48076.  $^{627d}$   
 $S_2[CH(C_6H_{13})COOH]_2$ , oil  $^{214}$   
 $S_2[CH(C_8H_{17})COOH]_2$ , m.  $37^\circ$ .  $^{214}$   
 $S_2[CH(C_{10}H_{21})COOH]_2$ , m.  $48^\circ$ .  $^{214}$ , 579  
 $S_2[CH(C_{12}H_{25})COOH]_2$ , m.  $56^\circ$ .  $^{214}$   
 $S_2[CH(C_{14}H_{27})COOH]_2$ , m.  $63^\circ$ .  $^{214}$   
 $S_2[CH(C_{16}H_{33})COOH]_2$ , m.  $72^\circ$ ,  $^{214}$   $71^\circ$ .  $^{210}$   
 $S_2[CH(CH_2Ph)COOH]_2$ , m.  $107^\circ$ .  $^{76}$   
 $S_2(CH_2CH_2COOH)_2$ , m.  $157^\circ$ ,  $^{382}$   $156^\circ$ ,  $^{393}$   $155^\circ$ ,  $^{75a}$ , 381d, 542,  $^{627a}$   $154^\circ$ ;  $^{775b}$  K 0.0090;  $^{491a}$  Et ester  $b_{17}$   $194^\circ$ ;  $^{627a}$  d 16/4 1.1532, d 25/4 1.1444; n 16/D 1.49650, n 25/D 1.49282;  $^{627d}$  amide, m.  $180^\circ$ .  $^{381d}$   
 $S_2(CH_2CH_2COSCH_2CH_2COOH)_2$ , m.  $134^\circ$ .  $^{381d}$   
 $S_2(CH_2CHMeCOOH)_2$ , m.  $87^\circ$ .  $^{461}$   
 $S_2(CH:CMecoOH)_2$ , m.  $194^\circ$ .  $^{511}$   
 $\alpha,\alpha'$ -Dithiodibutyrolactone, m.  $115^\circ$ .  $^{33}$   
 $S_2(CHMeCH_2COOH)_2$ , m.  $117^\circ$ .  $^{492}$   
 $S_2(ChEtCH_2COOH)_2$ , m.  $62^\circ$ .  $^{697}$   
 $S_2(CH_2CH_2CH_2COOH)_2$ , m.  $110^\circ$ ,  $^{382}$   $109^\circ$ ,  $^{32b}$ , 287, 750  $105^\circ$ ;  $^{775b}$  diamide, m.  $167^\circ$ .  $^{287}$   
 $S_2(CHMeCH_2CH_2COOH)_2$ , m.  $121^\circ$ .  $^{697}$   
 $S_2(CMe_2CH_2CH_2COOH)_2$ , m.  $85^\circ$ .  $^{750}$   
 $S_2[(CH_2)_4COOH]_2$ , m.  $90^\circ$ .  $^{697}$   
 $S_2[(CH_2)_5COOH]_2$ , m.  $83^\circ$ .  $^{399}$   
 $S_2[(CH_2)_{10}COOH]_2$ , m.  $106^\circ$ ,  $^{49}$   $92^\circ$ .  $^{166}$   
 $S_2[CH(COOMe)_2]_2$ , m.  $131^\circ$ .  $^{852}$   
 $S_2[CH(COOH)CH_2COOH]_2$ , L-acid, m.  $168^\circ$ ,  $[\alpha]$  17/D  $-272.9^\circ$  (absolute alcohol)  $-269.3^\circ$  (acetone),  $-290.5^\circ$  ( $H_2O$ ); D-acid, m.  $168^\circ$ ,  $[\alpha]$  17/D  $272.8^\circ$  (absolute alcohol)  $270.2$  (acetone).  $^{380d}$   
 $S_2[CH(COOH)CH_2CH_2CH_2COOH]_2$ , m.  $180^\circ$ .  $^{260}$   
 $S_2[CMe(COOH)_2]_2$ , N-methylamide, m.  $200^\circ$ , mono-*o*-toluide, m.  $208^\circ$ ; ditoluide *ortho*, m.  $174^\circ$ , *para*  $225^\circ$ .  $^{568}$   
 $PhSSCH_2CO_2Et$ ,  $b_{0.5}$   $90^\circ$ .  $^{401}$   
 $o-O_2NC_6H_4SSCH_2CO_2H$ , m.  $120^\circ$ .  $^{347}$   
 $o-O_2NC_6H_4SSCH(COMe)CO_2Et$ , m.  $83^\circ$ .  $^{347}$   
 $o-HOOC C_6H_4SSCH_2CO_2H$ , m.  $183^\circ$ .  $^{744}$

- $S_2(C_6H_4COOH-o)_2$ , m.  $302-5^\circ$ ,<sup>310</sup>  $289^\circ$ ,<sup>296a</sup>  $413$   $288^\circ$ ,<sup>622</sup>  $286^\circ$ ,<sup>305</sup>,  
<sup>447</sup>  $285^\circ$ ; <sup>395c</sup> piperidine salt, m.  $205-9^\circ$ ,<sup>15</sup>  $215.4$ ; <sup>18</sup> diMe ester,  
 m.  $132^\circ$ .<sup>305</sup>, <sup>310</sup>, <sup>416.7</sup>  
 $S_2(C_6H_4CONHEt-o)_2$ , m.  $203^\circ$ .<sup>46</sup>  
 $S_2(C_6H_4CONHCH_2Ph-o)_2$ , m.  $206^\circ$ .<sup>46</sup>  
 $S_2(C_6H_4CONHCOPh-o)_2$ , m.  $189^\circ$ .<sup>398</sup>  
 $[4,2-Cl(HOOC)C_6H_3]_2S_2$ , m.  $316-20^\circ$ ,<sup>350</sup>  $330^\circ$ .<sup>416.7</sup>  
 $[2,4,6-Cl_2(HOOC)C_6H_2]_2S_2$ , m.  $263^\circ$ ,<sup>350</sup>  $263.5^\circ$ .<sup>794</sup>  
 $[4,2-Br(HOOC)C_6H_3]_2S_2$ , m.  $310^\circ$ .<sup>563</sup>  
 $[5,2-O_2N(HOOC)C_6H_3]_2S_2$ , m.  $278^\circ$ ,<sup>763</sup>  $274^\circ$ ; diEt ester, m.  
 $179^\circ$ .<sup>731</sup>  
 $[2,3,6-(MeO)_2(HOOC)C_6H_2]_2S_2$ , m.  $185^\circ$ .<sup>677</sup>  
 $[3,4,2-(MeO)_2(HOOC)C_6H_2]_2S_2$ , m.  $129^\circ$ .<sup>677</sup>  
 $[4,2-H_2N(HOOC)C_6H_3]_2S_2$ , m.  $207.5^\circ$ ; diEt ester, m.  $197.5^\circ$ .<sup>850</sup>  
 $S_2(C_6H_4COOH-m)_2$ , m.  $242^\circ$ ,<sup>35</sup>  $246^\circ$ ; <sup>105</sup>, <sup>745</sup> amide, m.  $243^\circ$ .<sup>503</sup>  
 $[4,3-HO(HOOC)C_6H_3]_2S_2$ , m.  $236^\circ$ ,<sup>767</sup>  $245^\circ$ .<sup>417</sup>  
 $[2,4,5-(HO)_2(MeO_2C)C_6H_2]_2S_2$ , m.  $246^\circ$ ; di-2-Ac., m.  $214^\circ$ ; di-  
 2-Bz., m.  $192^\circ$ .<sup>407</sup>  
 $[2,5-H_2N(HOOC)C_6H_3]_2S_2$ , m.  $243^\circ$ ; diMe ester, m.  $149^\circ$ ,<sup>850</sup>  
 $194^\circ$ .<sup>96</sup>  
 $[4,3-H_2N(HOOC)C_6H_3]_2S_2$ , m.  $285^\circ$ .<sup>850</sup>  
 $S_2(C_6H_4COOH-p)_2$ , m.  $320^\circ$ ; <sup>35</sup> amide, m.  $278^\circ$ .<sup>503</sup>  
 $[3,4-HO(HOOC)C_6H_3]_2S_2$ , m.  $262^\circ$ .<sup>596</sup>  
 $S_2(C_6H_4CH_2CONHPh-o)_2$ , m.  $217^\circ$ .<sup>313</sup>  
 $[4,2-EtO(PhNHOCCH_2)C_6H_3]_2S_2$ , m.  $206^\circ$ .<sup>313</sup>  
 $S_2(C_6H_4OCH_2COOH-p)_2$ , m.  $147^\circ$ .<sup>529</sup>  
 $S_2(C_6H_4SCH_2COOH-p)_2$ , m.  $166.5^\circ$ .<sup>57</sup>  
 $[2,4-Me(HOOCCH_2O)C_6H_3]_2S_2$ , m.  $100^\circ$ .<sup>529</sup>  
 $[3,6,4-Me(Me_2CH)(HOOCCH_2O)C_6H_2]_2S_2$ , m.  $115^\circ$ .<sup>529</sup>  
 $\alpha$ - $[2,3-HO(MeO_2C)C_{10}H_5]_2S_2$ , diBz., m.  $262^\circ$ , with decomposi-  
 tion.<sup>407</sup>  
 $\alpha$ - $[4,3-HO(HOOC)C_{10}H_5]_2S_2$ , m.  $260^\circ$ .<sup>6</sup>

### Trisulfides, $R_2S_3$ and $Ar_2S_3$

- $Me_2S_3$ , m.  $-68.05^\circ$ ; <sup>79</sup> b.  $200^\circ$ ,<sup>128</sup>  $170^\circ$ ,<sup>435a</sup>  $165-70^\circ$ ,<sup>179</sup>  $b_4$   $42.5^\circ$ ,<sup>79</sup>  
 $41^\circ$ ,<sup>500</sup>  $b_{18}$   $54^\circ$ ,<sup>83</sup>  $b_{14}$   $62^\circ$ ,<sup>778a</sup>  $70^\circ$ ; <sup>113.7</sup>  $d_0$   $1.2162$ ,  $d_{10}$   $1.2059$ ,  
 $d_{17}$   $1.199$ ,<sup>435a</sup>  $d_{20}$   $1.2013$ ,  $d_{25}$   $1.1978$ ;  $n$   $20/D$   $1.6010$ ,<sup>79</sup>  $1.601$ .<sup>500</sup>  
 $Et_2S_3$ , m.  $-72.61^\circ$ ; <sup>79</sup>  $b_{0.1}$   $35-43^\circ$ ,<sup>87</sup>  $b_3$   $57^\circ$ ,<sup>79</sup>  $b_5$   $78^\circ$ ,<sup>81b</sup>  $b_{15}$   $85^\circ$ ,<sup>380b</sup>  
 $b_{25}$   $82^\circ$ ,<sup>113.7</sup>  $b_{26}$   $85^\circ$ ,<sup>477a</sup>  $92-7^\circ$ ; <sup>842</sup>  $d_{20}$   $1.1082$ ,<sup>79</sup>  $d$   $20/4$   $1.1140$ ; <sup>44</sup>,  
<sup>477a</sup>  $n$   $13/D$   $1.5689$ ,<sup>842</sup>  $n$   $15/D$   $1.56899$ ,<sup>477a</sup>  $n$   $20/D$   $1.5654$ ,<sup>79</sup>

- 1.56804; <sup>828</sup> surface tension 24.22°; parachor 335.3; <sup>44</sup> dipole moment  $1.64 \times 10^{-18}$ .<sup>842</sup>
- $\text{Pr}_2\text{S}_3$ ,  $b_{0.9}$  68–9°;  $n$  25/D 1.5424.<sup>129</sup>
- $i\text{-Pr}_2\text{S}_3$ ,  $b_5$  75–6°;  $n$  25/D 1.5351.<sup>129</sup>
- $\text{Bu}_2\text{S}_3$ , m. –77°;  $b_{0.9}$  90.5°;<sup>79</sup>  $b_{12}$  137–40°; <sup>113.7</sup>  $d_{20}$  1.0180;  $n$  20/D 1.5320.<sup>79</sup>
- $t\text{-Bu}_2\text{S}_3$ , m. 17.03°;  $b_4$  86°;<sup>79</sup>  $b_5$  85–7.5°; <sup>497</sup>  $d_{20}$  0.9922,  $d_{25}$  0.9881;  $n$  20/D 1.5225.<sup>79</sup>
- $(t\text{-C}_{12}\text{H}_{25})_2\text{S}_3$ ,  $d$  20/4 0.948.<sup>590</sup>
- $(\text{C}_{16}\text{H}_{33})_2\text{S}_3$ , m. 42.6°;<sup>34, 855</sup> 41.9°; <sup>72, 156</sup> dipole moment 1.63.<sup>855</sup>
- $(\text{C}_3\text{H}_5)_2\text{S}_3$ , (allyl),  $b$  188°;  $d_{15}$  1.012.<sup>490</sup>
- $(\text{C}_6\text{H}_{11})_2\text{S}_3$ , (cyclohexyl),  $n$  18/D 1.5884.<sup>229</sup>
- $(\text{Cl}_3\text{C})_2\text{S}_3$ , m. 57°.<sup>691</sup>
- $(\text{ClCH}_2\text{CH}_2)_2\text{S}_3$ , m. 31.5°;<sup>286</sup> 29°;<sup>650</sup> 27°; <sup>182, 429, 513</sup>  $b$  180–210°;<sup>169</sup>  $b_{0.3}$  110–2°;<sup>429</sup>  $b_5$  146.5°; <sup>513</sup>  $d$  30/4 1.3940; <sup>650</sup>  $n$  20/D 1.6110;<sup>286</sup>  $n$  30/D 1.6050.<sup>650</sup>
- $(\text{ICH}_2\text{CH}_2\text{CH}_2)_2\text{S}_3$ , m. 110°.<sup>182</sup>
- $(\text{CF}_3\text{CF}_2\text{CF}_2)_2\text{S}_3$ ,  $b$  153°;  $d$  31/4 1.6984;  $n$  31/D 1.3600.<sup>353</sup>
- $\text{Ph}_2\text{S}_3$ , m. 30°;<sup>44</sup> oil; <sup>810</sup>  $d$  20/4 1.418.<sup>44</sup>
- $(\text{MeC}_6\text{H}_4)_2\text{S}_3$ , *ortho* oil; <sup>810</sup> *para*, m. 82°;<sup>380c</sup> 77°.<sup>810</sup>
- $(\text{PhCH}_2)_2\text{S}_3$ , m. 49°.<sup>749</sup>
- $(\text{PhCH:CHCH}_2)_2\text{S}_3$ , m. 97.5°.<sup>493</sup>
- $(\text{C}_{10}\text{H}_7)_2\text{S}_3$ ,  $\alpha$  m. 75°;  $\beta$ , m. 109°.<sup>810</sup>
- $(2,5\text{-Cl}_2\text{C}_6\text{H}_3)_2\text{S}_3$ , m. 140°.<sup>116</sup>
- $(2,5\text{-Br}_2\text{C}_6\text{H}_3)_2\text{S}_3$ , m. 168°.<sup>116</sup>
- $(o\text{-O}_2\text{NC}_6\text{H}_4)_2\text{S}_3$ , m. 176°;<sup>468</sup> 174°;<sup>347, 494</sup> 185°.<sup>85c</sup>
- $o\text{-O}_2\text{NC}_6\text{H}_4\text{S}_3\text{C}_6\text{H}_4\text{OH-}p$ , m. 101.5°.<sup>347</sup>
- $(p\text{-O}_2\text{NC}_6\text{H}_4)_2\text{S}_3$ , m. 175°.<sup>347</sup>
- $(p\text{-H}_2\text{NC}_6\text{H}_4)_2\text{S}_3$ , m. 122°; <sup>375</sup> 2 HCl, m. 214.5°.<sup>698</sup>
- $[2,4,6\text{-AcNH}(\text{H}_2\text{N})_2\text{C}_6\text{H}_2]_2\text{S}_3$ , m. 221°.<sup>408</sup>
- $(4,3\text{-H}_2\text{NMeC}_6\text{H}_3)_2\text{S}_3$ , m. 90°; 2 HCl, m. 227°; diAc., m. 130°; diBz., m. 187°.<sup>368a</sup>
- $(2\text{-HO-}\alpha\text{-C}_{10}\text{H}_6)_2\text{S}_3$ , m. 118°.<sup>6</sup>
- $(1,4\text{-HOCl-}\beta\text{-C}_{10}\text{H}_5)_2\text{S}_3$ , m. 146°.<sup>303</sup>
- $(\text{HO}_2\text{CCH}_2)_2\text{S}_3$ , m. 124°; <sup>380b, 380c</sup> K 0.104.<sup>380b</sup>
- $(\text{HO}_2\text{CCHMe})_2\text{S}_3$ , m. 95°; <sup>491c</sup> K 0.080.<sup>491a</sup>
- $[(\text{MeO}_2\text{C})_2\text{CH}]_2\text{S}_3$ , m. 167°.<sup>852</sup>
- $(o\text{-HO}_2\text{CC}_6\text{H}_4)_2\text{S}_3$ , m. 304°; diEt ester, m. 110°.<sup>212</sup>
- $(p\text{-EtO}_2\text{CC}_6\text{H}_4)_2\text{S}_3$ , m. 52°.<sup>212</sup>
- $[4,3\text{-H}_2\text{N}(\text{HO}_2\text{C})\text{C}_6\text{H}_3]_2\text{S}_3$ , m. 207°; diAc., m. 95°.<sup>784</sup>

- $(\text{Ac}_2\text{CH})_2\text{S}_3$ , m.  $130^\circ$ .<sup>11</sup>  
 $\alpha$ -[3,4-Ac(HO)C<sub>10</sub>H<sub>5</sub>]<sub>2</sub>S<sub>3</sub>, m.  $192^\circ$ .<sup>6</sup>  
 $[(\text{PhS})_3\text{C}]_2\text{S}_3$ , m.  $99^\circ$ .<sup>30</sup>  
 $[(m\text{-MeC}_6\text{H}_4\text{S})_3\text{C}]_2\text{S}_3$ , m.  $82.5^\circ$ .<sup>30</sup>  
 $[(p\text{-MeC}_6\text{H}_4\text{S})_3\text{C}]_2\text{S}_3$ , m.  $119^\circ$ .<sup>30</sup>  
 $[(p\text{-}t\text{-BuC}_6\text{H}_4\text{S})_3\text{C}]_2\text{S}_3$ , m.  $114^\circ$ .<sup>30</sup>  
 $[2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{S})_3\text{C}]_2\text{S}_3$ , m.  $170.5^\circ$ .<sup>30</sup>  
 $[(p\text{-ClC}_6\text{H}_4\text{S})_3\text{C}]_2\text{S}_3$ , m.  $76^\circ$ .<sup>30</sup>

### Tetrasulfides, R<sub>2</sub>S<sub>4</sub> and ArS<sub>4</sub>

- $\text{Me}_2\text{S}_4$ , b<sub>1.5</sub>  $68\text{--}70^\circ$ ; d 25/d 1.3008; n 20/D 1.6621.<sup>286</sup>  
 $(\text{F}_3\text{C})_2\text{S}_4$ , b.  $135^\circ$ ; n 20/D 1.4608.<sup>350.5</sup>  
 $\text{Et}_2\text{S}_4$ , b.  $210\text{--}2^\circ$ ,<sup>137</sup> b<sub>0.1</sub>  $43\text{--}5^\circ$ ,<sup>229</sup>  $58\text{--}60^\circ$ ,  $65\text{--}7^\circ$ ,<sup>87</sup> b<sub>0.25</sub>  $62^\circ$  with decomposition,<sup>79</sup> b<sub>24</sub>  $106\text{--}8^\circ$ ,<sup>71</sup> b<sub>26</sub>  $109^\circ$ ; <sup>477a</sup> d 20/4 1.1616,<sup>71</sup> 1.1253;<sup>44</sup>, <sup>477a</sup> n 15/D 1.58436,<sup>477a</sup> n 19/D 1.6105,<sup>229</sup> n 20/D 1.6167, 1.6173,<sup>87</sup> 1.61809,<sup>71</sup> 1.6155,<sup>79</sup> 1.62086;<sup>328</sup> surface tension 24.54; parachor 406.4.<sup>44</sup>  
 $(\text{ClCH}_2\text{CH}_2)_2\text{S}_4$ , m.  $26.5^\circ$ .<sup>611</sup>  
 $\text{Pr}_2\text{S}_4$ , b<sub>11</sub>  $127\text{--}7.5^\circ$ ; d 20/4 1.1249; n 20/D 1.5904,<sup>71</sup> n 25/D 1.5993.<sup>726</sup>  
 $i\text{-Pr}_2\text{S}_4$ , b<sub>0.5</sub>  $88^\circ$ ; n 25/D 1.5812.<sup>129</sup>  
 $\text{Bu}_2\text{S}_4$  b<sub>0.1</sub>  $56^\circ$ ,<sup>87</sup> b<sub>1</sub>  $125\text{--}30^\circ$ ; d 20/4 1.0775; n 20/D 1.5705,<sup>71</sup> 1.5772,<sup>87</sup> 1.5722.<sup>79</sup>  
 $t\text{-Bu}_2\text{S}_4$ , m.  $2.33^\circ$ ; b<sub>0.2</sub>  $70^\circ$ ; d<sub>20</sub> 1.0690, d<sub>25</sub> 1.0640; n 20/D 1.5660.<sup>79</sup>  
 $\text{Am}_2\text{S}_4$ , oil.<sup>810</sup>  
 $i\text{-Am}_2\text{S}_4$ , b<sub>0.1</sub>  $56^\circ$ ; n 20/D 1.5542.<sup>87</sup>  
 $i\text{-Oct}_2\text{S}_4$ , d 20/4 1.0609; n 20/D 1.5482.<sup>71</sup>  
 $t\text{-Dodecyl}_2\text{S}_4$ , d 20/4 0.984.<sup>590</sup>  
 $(\text{C}_{16}\text{H}_{33})_2\text{S}_4$ , m.  $37.2^\circ$ ,<sup>34</sup>, <sup>855</sup>  $36.5^\circ$ ,<sup>156</sup>  $36^\circ$ ; <sup>72</sup> dipole moment 2.16.<sup>855</sup>  
 $(\text{H}_2\text{C:CHCH}_2)_2\text{S}_4$ , n 25/D 1.6360.<sup>726</sup>  
 $(\text{C}_6\text{H}_{11})_2\text{S}_4$ , b<sub>0.1</sub>  $100^\circ$ ; <sup>87</sup> d 18/4 1.209; n 18/D 1.6130,<sup>229</sup> n 20/D 1.6050.<sup>87</sup>  
 $\text{Ph}_2\text{S}_4$ , m.  $112^\circ$ ; <sup>839</sup> b<sub>0.1</sub>  $110^\circ$ .<sup>87</sup>  
 $(p\text{-MeC}_6\text{H}_4)_2\text{S}_4$ , m.  $75^\circ$ .<sup>380c</sup>, <sup>435a</sup>  
 $(\text{PhCH}_2)_2\text{S}_4$ , m.  $50^\circ$ .<sup>137</sup>, <sup>749</sup>  
 $(\alpha\text{-C}_{10}\text{H}_7)_2\text{S}_4$ , m.  $102^\circ$ .<sup>810</sup>  
 $(\beta\text{-C}_{10}\text{H}_7)_2\text{S}_4$ , m.  $101^\circ$ ,<sup>810</sup>  $85^\circ$ .<sup>137</sup>  
 $(p\text{-ClC}_6\text{H}_4)_2\text{S}_4$ , m.  $57^\circ$ .<sup>87</sup>



$(o\text{-O}_2\text{NC}_6\text{H}_4)_2\text{S}_4$ , m.  $116^\circ$ ,<sup>347</sup>  $160^\circ$ .<sup>85c</sup>

$(\text{HSCH}_2\text{CH}_2)_2\text{S}_4$ , m.  $128^\circ$ .<sup>137</sup>

$(\text{HO}_2\text{CCH}_2)_2\text{S}_4$ , m.  $113^\circ$ .<sup>380b, 380c</sup>

$(o\text{-HO}_2\text{CC}_6\text{H}_4)_2\text{S}_4$ , m.  $298^\circ$ .<sup>212</sup>

### Higher Sulfides

$\text{Et}_2\text{S}_5$ ,  $d_{18}$  1.233; <sup>671</sup> 2 isomers,  $b_{26}$   $119^\circ$ ;  $d$  16/4 1.1687,<sup>477a</sup>  $d$  20/4 1.1622; <sup>44</sup>  $n$  15/D 1.60269; <sup>477a</sup> surface tension 23.89; parachor 449; <sup>44</sup>  $b_{26}$   $130^\circ$ ,  $d$  16/4 1.1620,<sup>477a</sup>  $d$  20/4 1.1622; <sup>44</sup>  $n$  15/D 1.59517.<sup>477a</sup>

$\text{Pr}_2\text{S}_5$ ,  $d_{18}$  1.18.<sup>671</sup>

$(\text{H}_2\text{C}:\text{CHCH}_2)_2\text{S}_5$ ,  $d_{18}$  1.1249.<sup>801</sup>

$(\text{ClCH}_2\text{CH}_2)_2\text{S}_5$ ,  $d$  20/4 1.5013;  $n$  20/D 1.6853.<sup>286</sup>

$(o\text{-O}_2\text{NC}_6\text{H}_4)_2\text{S}_5$ , m.  $133^\circ$ .<sup>347</sup>

$(\text{CH}_2:\text{CHCH}_2)_2\text{S}_6$ , m.  $75.5^\circ$ .<sup>426</sup>

### Diselenides

$\text{Me}_2\text{Se}_2$ , b.  $155\text{--}7^\circ$ ,  $b_{21}$   $57^\circ$ .<sup>28</sup>

$\text{Et}_2\text{Se}_2$ , b.  $186^\circ$ ,<sup>642</sup>  $b_{44}$   $98^\circ$ ; <sup>678</sup>  $d$  20/4 1.2849,<sup>44</sup>  $d$  25/4 1.6772;  $n$  25/D 1.5806; <sup>678</sup> surface tension 24.63; parachor 316.4.<sup>44</sup>

$\text{Pr}_2\text{Se}_2$ ,  $b_{13}$   $99^\circ$ ,<sup>151</sup>  $b_{15}$   $103\text{--}4^\circ$ ; <sup>28</sup>  $d$  22.2/4 1.4991;  $n$  20/D 1.55535.<sup>151</sup>

$i\text{-Pr}_2\text{Se}_2$ , b.  $210^\circ$ .<sup>573.5</sup>

$\text{Bu}_2\text{Se}_2$ ,  $b_{8-8}$   $113\text{--}8^\circ$ ,<sup>776</sup>  $b_{13}$   $129\text{--}30^\circ$ ; <sup>28</sup>  $d$  20/4 1.390;  $n$  20/D 1.5399.<sup>776</sup>

$s\text{-Bu}_2\text{Se}_2$ ,  $b_{16}$   $130^\circ$ ;  $n$  20/D 1.5357.<sup>425</sup>

$t\text{-Bu}_2\text{Se}_2$ ,  $b_{3-4}$   $63\text{--}7^\circ$ ;  $d$  25/4 1.3529;  $n$  25/D 1.5351.<sup>678</sup>

$\text{Am}_2\text{Se}_2$ ,  $b_3$   $134\text{--}7^\circ$ ;  $d$  20/4 1.324;  $n$  20/D 1.5343.<sup>776</sup>

$i\text{-Am}_2\text{Se}_2$ ,  $b_3$   $134\text{--}7^\circ$ ;  $n$  20.5/D 1.5198.<sup>550</sup>

$\text{Hex}_2\text{Se}_2$ , m.  $-44^\circ$ ;  $b_3$   $150\text{--}2^\circ$ ;  $d$  20/4 1.258;  $n$  20/D 1.5246.<sup>776</sup>

$\text{Hep}_2\text{Se}_2$ , m.  $-11^\circ$ ,  $b_3$   $178\text{--}9^\circ$ ;  $d$  20/4 1.211;  $n$  20/D 1.5184.<sup>776</sup>

$\text{Oct}_2\text{Se}_2$ , m.  $-8^\circ$ ,  $b_3$   $197\text{--}205^\circ$ ;  $d$  20/4 1.175;  $n$  20/D 1.5142.<sup>776</sup>

$\text{Non}_2\text{Se}_2$ , m.  $10^\circ$ ;  $b_{0.12}$   $178\text{--}84^\circ$ ;  $d$  20/4 1.142;  $n$  20/D 1.5092.<sup>776</sup>

$(\text{C}_{12}\text{H}_{25})_2\text{Se}_2$ , m.  $21^\circ$ .<sup>191</sup>

$(\text{C}_{18}\text{H}_{37})_2\text{Se}_2$ , m.  $55^\circ$ .<sup>191</sup>

$\text{Ph}_2\text{Se}_2$ , m.  $63.5^\circ$ ,<sup>421, 449, 498</sup>  $63^\circ$ ,<sup>255, 359, 773</sup>  $62.5^\circ$ ,<sup>59</sup>  $62^\circ$ ,<sup>489, 787a, 787b,</sup> <sup>787d</sup>  $59^\circ$ ; <sup>44</sup>  $b_{11}$   $202\text{--}3^\circ$ .<sup>449</sup>

$(\text{PhCH}_2)_2\text{Se}_2$ , m.  $93^\circ$ ,<sup>601, 625</sup>  $90^\circ$ .<sup>277, 402, 779</sup>

$(o\text{-MeC}_6\text{H}_4)_2\text{Se}_2$ , m.  $26^\circ$ ;  $b_1$   $160\text{--}1^\circ$ ,<sup>423</sup>  $b_{13}$   $174\text{--}80^\circ$ .<sup>489</sup>

$(p\text{-MeC}_6\text{H}_4)_2\text{Se}_2$ , m.  $47^\circ$ .<sup>145, 787b</sup>

- $(p\text{-PhC}_6\text{H}_4)_2\text{Se}_2$ , m.  $184^\circ$ .<sup>662a</sup>  
 $(\alpha\text{-C}_{10}\text{H}_7)_2\text{Se}_2$ , m.  $88^\circ$ ,<sup>787a</sup>,  $787^\circ$   $88.5^\circ$ , metastable form, m.  $72^\circ$ .<sup>661</sup>  
 $(\beta\text{-C}_{10}\text{H}_7)_2\text{Se}_2$ , m.  $139.2^\circ$ ,<sup>661</sup> two forms, m.  $127^\circ$  and  $114^\circ$ .<sup>488</sup>  
 $(\text{ClCH}_2)_2\text{Se}_2$ , b<sub>1.5</sub>  $97^\circ$ .<sup>113</sup>  
 $(p\text{-ClC}_6\text{H}_4)_2\text{Se}_2$ , m.  $89^\circ$ ,<sup>144</sup>,  $254^\circ$ ,<sup>a</sup>  $663$   $86^\circ$ ;  $787^\circ$  b<sub>2</sub>  $192^\circ$ .<sup>254a</sup>  
 $(o\text{-ClC}_6\text{H}_4\text{CH}_2)_2\text{Se}_2$ , m.  $105.5^\circ$ .<sup>755a</sup>  
 $(p\text{-ClC}_6\text{H}_4\text{CH}_2)_2\text{Se}_2$ , m.  $82^\circ$ .<sup>755a</sup>  
 $(p\text{-BrC}_6\text{H}_4)_2\text{Se}_2$ , m.  $114.8^\circ$ ,<sup>663</sup>  $115^\circ$ ,<sup>254a</sup>  $108^\circ$ ,<sup>787b</sup>  $113^\circ$ .<sup>144</sup>  
 $(p\text{-BrC}_6\text{H}_4\text{CH}_2)_2\text{Se}_2$ , m.  $106^\circ$ .<sup>755a</sup>  
 $o\text{-O}_2\text{NC}_6\text{H}_4\text{Se}\cdot\text{SePh}$ , m.  $56^\circ$ .<sup>662b</sup>  
 $(o\text{-O}_2\text{NC}_6\text{H}_4)_2\text{Se}_2$ , m.  $212^\circ$ ,<sup>662b</sup>  $209^\circ$ ,<sup>47</sup>,  $95^\circ$  b<sub>2</sub>  $210^\circ$ ,<sup>667</sup>  $206.5^\circ$ ,<sup>93</sup>  $211^\circ$ .<sup>662a</sup>  
 $(m\text{-O}_2\text{NC}_6\text{H}_4)_2\text{Se}_2$ , m.  $83^\circ$ ,<sup>636</sup>  $81^\circ$ .<sup>254b</sup>  
 $(p\text{-O}_2\text{NC}_6\text{H}_4)_2\text{Se}_2$ , m.  $179^\circ$ .<sup>662a</sup>  
 $[2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3]_2\text{Se}_2$ , m.  $265^\circ$ .<sup>277</sup>  
 $[3,4\text{-O}_2\text{N(H}_2\text{N)}\text{C}_6\text{H}_3]_2\text{Se}_2$ , m.  $169^\circ$ .<sup>144</sup>  
 $(2,4\text{-O}_2\text{NMeC}_6\text{H}_3)_2\text{Se}_2$ , m.  $178^\circ$ ,<sup>667</sup>  $70^\circ$ .<sup>144</sup>  
 $(2,5\text{-O}_2\text{NMeC}_6\text{H}_3)_2\text{Se}_2$ , m.  $205^\circ$ .<sup>662b</sup>  
 $(3,4\text{-O}_2\text{NMeC}_6\text{H}_3)_2\text{Se}_2$ , m.  $150^\circ$ .<sup>144</sup>  
 $(o\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2)_2\text{Se}_2$ , m.  $103.5^\circ$ .<sup>625</sup>,  $755^\circ$  b  
 $(m\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2)_2\text{Se}_2$ , m.  $106^\circ$ .<sup>625</sup>  
 $(5,2\text{-O}_2\text{NCIC}_6\text{H}_3\text{CH}_2)_2\text{Se}_2$ , m.  $171.5^\circ$ .<sup>755a</sup>  
 $(p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2)_2\text{Se}_2$ , m.  $107.5^\circ$ .<sup>625</sup>  
 $(p\text{-HOC}_6\text{H}_4)_2\text{Se}_2$ , m.  $134^\circ$ ; diAc., m.  $90.5^\circ$ .<sup>421</sup>  
 $(p\text{-EtOC}_6\text{H}_4)_2\text{Se}_2$ , m.  $65^\circ$ .<sup>787b</sup>  
 $(\text{H}_2\text{NCH}_2\text{CH}_2)_2\text{Se}_2$ , 2HCl, m.  $188^\circ$ .<sup>163</sup>  
 $(o\text{-H}_2\text{NC}_6\text{H}_4)_2\text{Se}_2$ , m.  $83^\circ$ ,<sup>422</sup>  $81^\circ$ ;  $47$  2HCl, m.  $202^\circ$  with decomposition; diAc., m.  $167.5^\circ$ ;  $422$  diformate, m.  $174^\circ$ .<sup>154</sup>  
 $(o\text{-MeNHC}_6\text{H}_4)_2\text{Se}_2$ , m.  $89^\circ$ ; diformate, m.  $104^\circ$ ; diBz., m.  $170^\circ$ .<sup>154</sup>  
 $(m\text{-H}_2\text{NC}_6\text{H}_4)_2\text{Se}_2$ , 2HCl, m.  $292^\circ$  with decomposition; diAc., m.  $186^\circ$ .<sup>636</sup>  
 $(p\text{-H}_2\text{NC}_6\text{H}_4)_2\text{Se}_2$ , m.  $80^\circ$ ,<sup>41</sup>  $79.5^\circ$  with decomposition;  $422$  diAc., m.  $205^\circ$ ,<sup>639</sup>  $143^\circ$ ;  $41$  diBz., m.  $267^\circ$ ; dicaproate, m.  $177^\circ$ ; dival-  
 erate, m.  $123^\circ$ .<sup>639</sup>  
 $(2,4\text{-H}_2\text{NMeC}_6\text{H}_3)_2\text{Se}_2$ , m.  $95^\circ$ .<sup>422</sup>  
 $(2,6\text{-H}_2\text{NMeC}_6\text{H}_3)_2\text{Se}_2$ , m.  $134^\circ$ .<sup>422</sup>  
 $(\beta\text{-C}_{14}\text{H}_7\text{O}_2)_2\text{Se}_2$ , (anthraquinoyl), m.  $260^\circ$ .<sup>662b</sup>  
 $\text{Se}_2(\text{CH}_2\text{COOH})_2$ , m.  $101^\circ$ ,<sup>58</sup>,  $261^\circ$  b<sub>1</sub>  $100^\circ$ ;  $601$   $K_1$   $4.86 \times 10^{-4}$ ,  $K_2$   $0.640 \times 10^{-4}$ .<sup>261b</sup>

- $\text{Se}_2(\text{CHMeCOOH})_2$ , 2 forms, m.  $109.5^\circ$ ;  $d_{15}$  2.005,  $K_1$   $3.77 \times 10^{-4}$ ,  $K_2$   $0.449 \times 10^{-4}$ ; m.  $88^\circ$ ;  $d_{25}$  1.982; D- m.  $87.5^\circ$ ;  $d_{25}$  2.024;  $K_1$   $3.75 \times 10^{-4}$ ,  $K_2$   $0.446 \times 10^{-4}$ ; L m.  $87.5^\circ$ ; *meso*, m.  $73^\circ$ ,  $d_{25}$  2.016;  $K_1$   $3.89 \times 10^{-4}$ ,  $K_2$   $0.447 \times 10^{-4}$ .<sup>261b</sup>  
 $\text{Se}_2(\text{CHEtCOOH})$ , DL,  $K_1$   $4.30 \times 10^{-4}$ ,  $K_2$   $0.481 \times 10^{-4}$ ; D & L, m.  $52^\circ$ .<sup>261b</sup>  
 $\text{Se}_2(\text{CHiPrCOOH})_2$ , m.  $122^\circ$ .<sup>261a</sup>  
 $\text{Se}_2(\text{CHPhCOOH})_2$ , D-, m.  $165^\circ$ .<sup>261b</sup>  
 $\text{Se}_2(\text{CH}_2\text{CH}_2\text{COOH})_2$ , m.  $137^\circ$ ,<sup>261b</sup>  $135.5^\circ$ ;<sup>601</sup>  $K_1$   $1.013 \times 10^{-4}$ ,  $K_2$   $0.156 \times 10^{-4}$ .<sup>261b</sup>  
 $\text{Se}_2(\text{CH}(\text{COOH})\text{CH}_2)_2$ , m.  $176^\circ$ .<sup>261b</sup>  
 $\text{Se}_2(\text{C}_6\text{H}_4\text{COOH-}o)_2$ , m.  $295^\circ$ ,<sup>684</sup>  $297^\circ$ ; <sup>123, 474</sup>  $-\text{COCl}$ , m.  $174^\circ$ ; amide, m.  $266^\circ$ ; diMe ester, m.  $144^\circ$ ; diEt ester, m.  $130^\circ$ .<sup>474</sup>  
 $\text{Se}_2(\text{C}_6\text{H}_4\text{COOH-}m)_2$ , m.  $265^\circ$ .<sup>35</sup>  
 $\text{Se}_2(\text{C}_6\text{H}_4\text{COOH-}p)_2$ , m.  $297^\circ$ ,<sup>297</sup>  $296^\circ$ .<sup>35</sup>

### Seleno-Sulfides <sup>662a</sup>

- $\text{C}_{18}\text{H}_{33}\text{SSeC}_6\text{H}_4\text{NO}_2\text{-}o$ , m.  $52^\circ$ .  
 $\text{PhSSeC}_6\text{H}_4\text{NO}_2\text{-}o$ , m.  $55^\circ$ .  
 $\text{PhCH}_2\text{SSeC}_6\text{H}_4\text{NO}_2\text{-}o$ , m.  $54.6^\circ$ .  
 $p\text{-MeC}_6\text{H}_4\text{SSeC}_6\text{H}_4\text{NO}_2\text{-}o$ , m.  $87^\circ$ .  
 $\alpha\text{-C}_{10}\text{H}_7\text{SSeC}_6\text{H}_4\text{NO}_2\text{-}o$ , m.  $111.3^\circ$ .  
 $\beta\text{-C}_{10}\text{H}_7\text{SSeC}_6\text{H}_4\text{NO}_2\text{-}o$ , m.  $87.8^\circ$ .  
 $o\text{-NO}_2\text{C}_6\text{H}_4\text{SSeC}_6\text{H}_4\text{NO}_2\text{-}o$ , m.  $198.2^\circ$ .  
 $t\text{-BuSSeC}_6\text{H}_4\text{NO}_2\text{-}p$ , m.  $75.5^\circ$ .  
 $\text{MeCH}_2\text{CMe}_2\text{SSeC}_6\text{H}_3\text{NO}_2\text{Cl-}2,4$ , m.  $32.7^\circ$ .  
 $\text{C}_{12}\text{H}_{25}\text{SSeC}_6\text{H}_3\text{NO}_2\text{Cl-}2,4$ ,  $57.5^\circ$ .  
 $(\text{CH}_2\text{SSeC}_6\text{H}_3\text{NO}_2\text{Cl-}2,4)_2$ , m.  $202^\circ$ .  
 $\text{CH}_2(\text{CH}_2\text{SSeC}_6\text{H}_3\text{NO}_2\text{Cl-}2,4)_2$ , m.  $148.6^\circ$ .  
 $t\text{-BuSSeC}_6\text{H}_3\text{NO}_2\text{Br-}2,4$ , m.  $57.3^\circ$ .  
 $\text{PhCH}_2\text{SSeC}_6\text{H}_3\text{NO}_2\text{Br-}2,4$ , m.  $71.2^\circ$ .  
 $p\text{-MeC}_6\text{H}_4\text{SSeC}_6\text{H}_3\text{NO}_2\text{Br-}2,4$ , m.  $99.7^\circ$ .  
 $\text{C}_{18}\text{H}_{37}\text{SSeC}_6\text{H}_3\text{NO}_2\text{Me-}2,4$ , m.  $67.3^\circ$ .  
 $c\text{-HexSSeC}_6\text{H}_3\text{NO}_2\text{Me-}2,4$ , m.  $77.5^\circ$ .  
 $\text{MeSSeC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4$ , m.  $106.5^\circ$ .  
 $\text{EtSSeC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4$ , m.  $105^\circ$ .  
 $\text{Me}_2\text{CHSSeC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4$ , m.  $77^\circ$ .  
 $t\text{-BuSSeC}_6\text{H}_4\text{Ph-}p$ , m.  $69.5^\circ$ .  
 $\text{Ph}_3\text{CSSeC}_6\text{H}_4\text{Ph-}p$ , m.  $122.5^\circ$ .  
 $\text{PhSeSPh}$ , m.  $58^\circ$ .

PhSeSC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*o*, m. 58.8°.

PhSeSC<sub>10</sub>H<sub>7</sub>- $\alpha$ , m. 60.5°.

$\alpha$ -C<sub>10</sub>H<sub>7</sub>SeSC<sub>6</sub>H<sub>3</sub>NO<sub>2</sub>Cl-2,4, m. 143.5°.

### Three Sulfur and Selenium Atoms

Et<sub>2</sub>Se<sub>3</sub>, b<sub>26</sub> 100°; d 13/4 1.7805; n 12.8/D 1.60919.<sup>477b</sup>

Et<sub>2</sub>S<sub>2</sub>Se, b<sub>13</sub> 94°; d 13/4 1.4094,<sup>477b</sup> d 20/4 1.3881; <sup>44</sup> n 12.8/D 1.57914; <sup>477b</sup> surface tension 24.25; parachor 350.2.<sup>44</sup>

Et<sub>2</sub>Se<sub>2</sub>S, b<sub>26</sub> 98°; d 13/4 1.7070,<sup>477b</sup> d 20/4 1.6957; <sup>44</sup> n 12.8/D 1.60244; <sup>477b</sup> surface tension 24.84; parachor 264.0.<sup>44</sup>

Ph<sub>2</sub>S<sub>2</sub>Se, m. 51°; d 20/4 1.593.<sup>44</sup>

Ph<sub>2</sub>Se<sub>2</sub>S, m. 55°; d 20/4 1.873.<sup>44</sup>

(*o*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Se<sub>2</sub>S, m. 170.5°.<sup>662b</sup>

(2,4-O<sub>2</sub>NC<sub>6</sub>H<sub>3</sub>)<sub>2</sub>Se<sub>2</sub>S, m. 198°.<sup>662b</sup>

(2,5-O<sub>2</sub>NMeC<sub>6</sub>H<sub>3</sub>)<sub>2</sub>Se<sub>2</sub>S, m. 154.6°.<sup>662b</sup>

[2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>Se<sub>2</sub>S, decomposes 256°.<sup>662b</sup>

(2,3,5-HOBrMeC<sub>6</sub>H<sub>2</sub>)<sub>2</sub>S<sub>2</sub>Se, m. 98°.<sup>69</sup>

( $\beta$ -C<sub>14</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>Se<sub>2</sub>S, (anthraquinoyl), m. 242°.<sup>662b</sup>

### Higher mixed Selenide-Sulfides-Telurides

(EtS)<sub>2</sub>Se:S, b. 102°.<sup>44</sup>

(EtS)<sub>2</sub>S:Se, b. 105°.<sup>44</sup>

(EtSe)<sub>2</sub>Se:S, b. 104°.<sup>44</sup>

(EtSe)<sub>2</sub>S:Se, b. 107°.<sup>44</sup>

(MeOC<sub>6</sub>H<sub>4</sub>TeS)<sub>2</sub>S, m. 61°.<sup>679</sup>

(EtOC<sub>6</sub>H<sub>4</sub>TeS)<sub>2</sub>S, m. 114°; penta sulfide, m. 92°.<sup>679</sup>

(HO<sub>2</sub>CCHMeS)<sub>2</sub>Te, m. 114°.<sup>69</sup>

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